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ASPECTS OF SUSTAINABLE DEVELOPMENT: FLY ASH DEPOSITS, BIOSOLIDS, CONTAMINATED BIOMASS

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ABSTRACT. Nowadays, barren and inert fly ash deposits result from power plants operating on fossil coal and occupy large areas of land. They change the landscape, altering ecosystems and dispersing pollutants by precipitations and deflations. On the other hand, from wastewater treatment results sludge waste (biosolids) rich in nutrients. Biosolids are fertilizers with many nutrients and could be recycled to improve soil productivity and stimulate plant growth. A solution was found for the capitalization of two wastes - biosolids and fly ash, both resulting in the same city, Timisoara, Romania. The use of biosolids in fly ash fertilization provides rapid efficiency in topsoil for plant growth. Plant species were chosen considering the possibilities to restrict the metal access in plants, *i.e. Lolium perenne* species*,* with reduced harvest, recycled as fodder or, on the contrary, to stimulate accumulation of metals *i.e. Onobrychis viciifolia* species*,* with increased harvest, but potentially toxic biomass, processes evidenced by a specific parameter, the coefficient of translocation. Pilot experiments was done in four versions, each in three replicates in a randomized block. The treatment were control and fertilized variant fot each plant species. The new crop installed presents characteristics depending on plant species: with accumulation of metals, i.e. Cr, Cu, Ni, in the shoots, such as in leguminous *Onobrychis viciifolia* species, resulting vegetation with waste regime. with smaller accumulations of heavy metals, such of grass *Lolium perenne,* with recycling possibilities in agro-zoo technical field.

Keywords: *biosolids, fly ash deposits, heavy metal bioavailability, Lolium perenne, Onobrychis viciifolia.*

INTRODUCTION

Thermal power plants operating on coal are the main sources of energy worldwide. Coal combustion produces solid residues resulting from the non-combustible fraction. Physical and chemical characteristics of residues are determined by the nature of coal used in combustion, by operating conditions and post combustion conditions [1-3]. Coal combustion leads to the formation in

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time of huge wastes in the open - fly ash deposits. In coal combustion, about 70÷75% of the obtained fly ash is stored either on specially designated landfill (deposits) or in natural depressions [1,4]. These sites are devoid of vegetation, have the appearance of a deserted area and have the potential of spreading material in the form of fine particles in the atmosphere and/or soil, leaching, water percolation etc. [5-6]. Some stabilization/ remediation strategies using plant were developed. The process is simple, but several necessarily stages are required [7-11]. From municipal wastewater plants, results in large quantities, another waste material - the sewage sludge (biosolids), with high nutrient content. The disadvantages of biosolids use are due to smell, potential disease risk to humans or animals that are consumers of products/food from treated fields. Municipal sludge is stabilized (higienically) by one or more controlled processes, aerobic, anaerobic, liming, etc., to reduce pathogens and to remove the vectors drawn here: flies, rodents, birds etc. [12-13]. The literature reports that these biosolids may have an average content in nitrogen between 1 and 6%: low N content (1÷3% N), or high N content (3÷6% N) (while the manure contains 1.2÷4% N) and 1.5 P% (while the manure contains 0.3÷3.3%) [12]. The biosolids contain also other useful microelements like Fe, Mn, S, Ca, Mg, K, etc. [13-15]. Biosolids can be used in fertilizing forests, contaminated soil for phyto-remediation of the sterile materials deposits. Upper inert fly ash deposits are treated in advance to ensure a minimum nutrient, needed for the installation of healthy vegetation [15-19].

The aim of the study is to form on fly ash deposits a plant layer for particulate matter stabilization and furthermore for ecological restoration, by choosing proper plant species that generate biomass with recycling possibilities. Fly ash deposits of Timisoara, Romania, occupy hundreds of hectares of land with a moon aspect and with high risk of deflation, erosion, and leaching of stored material The whole process involves the use of another waste, available in large quantities, the municipal sludge. Also, from the Timisoara municipal water treatment plant, three tons of municipal sludge with 20% dries matter, or 12 tons with 5% dry matter result daily. Until now, for the two types of waste there is no sustainable management for recovery or ecological integration in the environment. In this paper we performed a research to integrate in the upper layers of fly ash deposits a pre-determined quantity of semi liquid biosolids for phytostabilization/phytoremediation of inert waste. The choices of plant species for this study were made either to lead to high biomass yields with metals bioaccumulated into, *i.e.* leguminous *Onobrychis viciifolia,* or to obtain reduced biomass including low quantities of metals, *i.e. Lolium perenne*. Pilot experiments was done in four versions, each in three replicates in a randomized block. The treatment were control and fertilized variant fot each plant species.

MATERIALS AND METHODS

Fly ash samples and biosolids analysis was done to determine the metal concentrations to according with the Romanian standardized methodology. 5g soil samples analysis (in triplicate) was done to determine the metals concentrations. Metals were extracted from the soil samples by heating with Aqua Regia for 2hrs, at reflux. After interrupting the heat, the system was left in stand-by for 16 hrs. Then the samples were diluted in a calibrated flask with deionized water to 50 ml. Plant sampling was done in agreement with the Romanian standardized methodology. Plant tissues were thoroughly washed with de ionized water to remove any soil particles attached to plant surfaces. 5g plant tissues were dried (105°C) to constant weight. Plant samples with precise weight are then brought to 550°C; to the residual materials 5ml of concentrated hydrochloric acid are added, samples are maintained 30 minutes on the dry sand bath. After filtering those in a paper filter with small porosity (type 640de Mackerel-Nagel Germany), were taken to a calibrated flask (25 mL) with hydrochloric acid 1:1 solution. Plant and soil extracts analysis was done using a spectrophotometer, Avanta AAS. The detection limit of the device for Cr, Cu, Fe, Mn, and Zn is of 0.05mg/L, for Ni is of 0.10 mg/L, for Pb is of 0.20 mg/L. The following were determined according to Romanian current laws: pH, DM, N_{Total} and P. The vegetation degree of coverage is established by Braun-Blanquet scale [18]. For in time monitoring of the metal bioaccumulation in the aerial parts of plants and the level of metals in upper layer of fly ash deposit, we analyzed: [18, 20-22]: 1. The amount of metals accumulated in aerial plant tissue, 2. The coefficient of metal translocation from roots to shoot of plants $TC = Q_S/Q_R$, where: Q_S - metal amount in the aerial tissue (mg/ kg D.M.), Q_R - amount of metal in roots (mg/ kg D.M.).

RESULTS AND DISCUSSION

1. Strategy research on experimental parcels

The study is carried out on four different experiments: 1. Non-treated fly ash parcel seeded with *Lolium perenne* grass species (C1); 2. Non-treated parcel fly ash seeded with *Onobrychis viciifolia* species (C2); 3. Fly ash parcel fertilized with municipal sludge (25 to/ha DM) and seeded with *Lolium perenne* grass species (C3); 4. Fly ash parcel fertilized with municipal sludge (25 to/ha DM) and seeded with *Onobrychis viciifolia* leguminous species (C4). The experimental parcels are randomized in an experimental block area. Each experimental parcel is carried out in triplicates. The area of each experimental parcel was 10 m^2. Agricultural work is done with ordinary farm equipment to prepare the experimental parcels for sowing, fertilization, and for plants harvesting. Was initiated and maintained a plant cover of grasses and leguminous species adapted to excessive drought conditions.

Harvesting and management of resulting biomass were done in concordance with their quality indicators.

2. Characterization of fly ash and biosolids

2.1. Fly ash characterization

From fossil coal combustion in power plants of Timisoara city, result the non-combustible fraction, fly ash. A field study was conducted at fly ash deposit during three years to assess the effect of biosolids treatment. Metal content of the upper layer of experimental parcels is presented in Table 1. C1 and C2 parcels correspond to fly ash experimental variants without biosolids and C3 and C4 parcels correspond to fertilized fly ash with organic fertilizer, biosolids. Fly ash has pH = 7.2 and does not contain nutrients, nitrogen and phosphorus; carbon content is present but in non-biodegradable form.

Table 1. Concentration of metals of the upper layer of experimental parcels; Values are means of 3 replicate samples±SE

No	Parcel	* Heavy metal content in the topsoil upper layer [mg/kg D.M.]						
		Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	C1	64.2±1.1	72.4±2.5	1,860.0±20.2	150.0±3.6	68.6±2.4	19.6±3.1	124.0±2.5
2	C2	93.6±3.6	77.6±2.1	1,903.0±21.9	153.1±4.4	68.8±2.2	7.4±0.4	82.6±2.1
3	C3	99.0±2.3	74.2±2.9	1,878.0±11.7	150.0±4.6	54.6±1.7	28.5±3.8	122.7±3.5
4	C4	99.6±2.4	82.0±2.0	1,892.0±12.2	171.2±4.3	60.1±1.9	7.3±0.7	79.5±1.8

* mean values

2.2. Biosolids characterization

Biosolids result from Timisoara municipal water treatment plant. 25 to/ha D.M. of biosolids, having characteristics presented in Table 2, were used to prepare the fertile layer of vegetation covering the fly ash deposits, in Timisoara's vicinity. Other characteristics of biosolids: humidity= 90±0.5%, organic matter=26.4±0.6%, N_{Total} =2.5±0.2%, P=0.35±0.2%, pH = 7.1±0.3.

Table 2. Heavy metal content of used biosolids. Values are means of 12 samples±SE

Material	*Heavy metal content of used biosolids [mg/kg D.M]							
	Cr_{tot}	Cu	Cd	Fe	Mn	Ni	Pb	Zn
Biosolids	134.7±3.2	333.9±3.5	7.3±0.1	2,003.7±12.2	75.0 ±1.8	27.4 ±0.3	157.8±12.0	304.6±13.6

* mean values

2.3. *Influence of fly ash with biosolids mixture on the mobilization of metals in parts of plants (roots and shoots)*

Vegetation strategy is selected for plant species leading to large amount of biomass, which contains in mature plants (harvested) bioaccumulated metals, or plant species leading to lower amounts of biomass and, as well, a lower level of accumulation of metals in the aerial parts. Because of the new vegetative cycle after harvesting, the young plants grown on non-treated soil will selectively accumulate metals in tissues, namely in the aerial parts. In Table 3 are presented the surfaces covered with plants and the amount of green mass harvested from cultivated experimental parcels.

Table 3. The biomass quantities and coverage degree based on Braun-Blanquet scale [18]

No	*n	Parcel	Plant species	**Biomass quantity [kg/ha]	Coverage degree (Braun-Blanquet scale)
1	3	C1	*Lolium perenne*	805.0 ±25.1	Level 2 small abundance, limited coverage degree 5-25%;
2	3	C2	*Onobrychis viciifolia*	25.0 ±3.2	Level 1 more individuals, but with small coverage degree under 5%;
3	3	C3	*Lolium perenne*	1,125.0 ±132.5	Level 4 abundant individuals and good coverage degree 50-75%;
4	3	C4	*Onobrychis viciifolia*	11,960.0 ±154.9	Level 4, abundant individuals, good coverage degree 50-75%;

* number of observations,* * mean values

The species *Lolium perenne* covers non-fertilized fly ash layer, C1, at level of coverage 2 on the Braun-Blanquet scale, up to 25%, the sown area. If the fly ash layer is fertilized with biosolids, C3, coverage with plants is higher, reaching level 4 on the Braun-Blanquet scale, but the quantity of biomass harvested from this experimental version is lower, about 1,125.0 kg/ha of green biomass. *Onobrychis viciifolia,* a leguminous species, did not grow on non-fertilized fly ash parcel, C2. Grown plants dry slowly. Fertilization of fly ash experimental parcels with biosolids, C4, determined the growth of a vegetable layer covering over 50% of the the sown area. This layer produced a quantity of plant biomass over 10 times higher than that obtained when grasses *Lolium perenne* was cultivated.

In Tables 4 and 5 are shown the amounts of metal accumulated in plant tissue at maturity (1st harvested biomass in July) and in young plants in the moment of the new vegetative cycle after harvesting.

The two species of plants grown on non fertilized experimental parcels accumulate in their mature phenophase similar amounts of heavy metals i.e.: Cu, Cr, Fe, Ni and Pb. Other hand, *Onobrychis viciifolia* species accumulates two times more Mn and 4 times more Zn versus *Lolium perenne* species. The addition of organic fertilizer has determined that grass species accumulate lower amounts of metals, Cr, Fe and Zn up to 2 times lower, of Cu up to 4 times lower and Pb up to 12 times, versus the amount that was found in plants grown on untreated fly ash experimental parcel.It can be seen, from Table 4, that depending on the nature of the plant, accumulation of Cu, Fe, Pb, and Ni is 2-3 times higher than the amounts accumulated in mature plants.

Table 4. Metal content, in harvested biomass, mg/kg D.M.

* n	Parcel	Plant species	* * Metal content in (1st harvested biomass in July) [mg/kg D.M.]						
			Cr	Cu	Fe	Mn	Ni	Pb	Zn
3	C1	***Lolium perenne***	3.5 ±0.6	1.9 ±0.5	377.9 ±13.8	13.9 ±0.5	1.8 ±0.3	1.2 ±0.3	17.9 ±1.2
3	C2	***Onobrychis viciifolia***	3.4 ±0.6	1.8 ±0.6	378.0 ±15.7	25.0 ±0.8	1.6 ±0.3	1.3 ±0.3	19.2 ±2.2
3	C3	***Lolium perenne***	1.5 ±0.4	1.5 ±0.6	207.2 ±12.4	29.3 ±1.6	5.0 ±0.7	0.1	9.5 ±2.5
3	C4	***Onobrychis viciifolia***	3.7 ±0.6	2.5 ±0.7	199.6. ±12.2	35.5 ±2.5	7.5 ±0.9	0.2 ±0.1	12.0 ±2.7

* number of observations,* * mean values

In contrast, plants bio accumulate Mn and Ni up to 2 times more than in plant tissues grown on non-treated topsoil experimental parcel. If leguminous plants grown on treated experimental parcel with biosolids, bioaccumulation of heavy metals increases between 2-10 times for the quantity of most heavy metals accumulated in tissues versus plants grown on non-treated experimental parcels. There is one exception - lead; in this case, the bioaccumulation decreases in the aerial plant tissues. In conclusion, plants from grass species grown on experimental parcels fly ash fertilized with biosolids led to: 1) green mass productivity 10 times lower than leguminous species, 2) instead, grass species present lower degree of bioaccumulation of toxic metals like Cr and Pb, than leguminous species of plants, 3) the accumulation in the aerial part of the species *Lolium perenne* for Fe, Mn and Ni metals is within normal limits for grassland plants.

Plants grown on experimental parcels, fly ash fertilized with biosolids, in the vegetative phenophase, a new cycle, after harvesting, have significant differences in the degree of accumulation of toxic metals; addition of organic fertilizer led to a similar behaviour in the case of grass species for both phenophases analyzed in terms of quantities of metal bioaccumulations, see Table 5. The addition of organic fertilizer on the experimental parcels fly ash resulted in different behaviours regarding the bioaccumulation of heavy metals on the different phenophases in leguminous species, namely young plants accumulate 3-4 times larger amounts of Cr, Cu, Fe, Ni versus the bioaccumulation of heavy metals in tissues of mature plants. The accumulation of metals in this species, both in young and mature plants, is several times larger than in the case of grass species, *i.e.* the addition of fertilizer limits the access of Pb in aerial tissues.

Table 5. Metal content, of young plant (the new vegetative cycle)

* n	Parcel	Plant species	* * Metal content (in new vegetative cycle) [mg/kg D.M.]						
			Cr	Cu	Fe	Mn	Ni	Pb	Zn
3	C1	***Lolium perenne***	4.5 ±0.5	4.5 ±0.2	672.5 ±32.6	15.2 ±3.7	7.2 ±0.5	2.8	25.5±2.5
3	C2	***Onobrychis viciifolia***	1.7 ±0.2	2.5 ±0.3	672.1 ±31.7	32.9 ±7.5	7.2 ±0.5	2.9	25.0±2.3
3	C3	***Lolium perenne***	1.6 ±0.2	4.3 ±0.3	312.5 ±22.3	65.4 ±6.5	5.7 ±0.7	-	44.8±3.3
3	C4	***Onobrychis viciifolia***	11.6 ±0.7	12.2±0.8	1,784.4 ±45.6	70.3 ±7.8	18.9±0.9	-	45.0±5.1

* number of observations,* * mean values

In figures 1 and 2, the translocation of metals from the roots in the shoots of the plant is presented. The means of translocation depend on many factors like: nature of plant species, plant phenophase development, the nature of soil and type of fertilization treatment thereof.

The two plant species selected for fly ash deposits vegetation allow passage of a limited amount of total metal accepted in root at maturity stage. Generally, the aerial part of plants accumulates small amounts of metal, so the translocation coefficient is lower than 1. Plants grown on non-fertilized fly ash have a TC between 0.17 and 0.5. An exception is in the case of lead where the amount of metal accumulated in the aerial part of plants exceeds 3 times the amount of metal accumulated in root. Addition of biosolids fertilizer determined to a series of metals the reducing of TC. But nickel ion is translocated in much higher quantity in *Lolium perenne* plants grown on experimental parcels fly ash fertilized. In the case of *Onobrychis viciifolia* young plants, biosolids addition determined the increase of translocation coefficient values by 6-9 times for some metals, like Pb, Zn, and Ni.

The addition of biosolids in the soil alters metal species availability, which then translocate and accumulate in the aerial part of plants. In *Lolium perenne* plants grown on experimental parcels fly ash treated with biosolids, in both phenophases, translocation coefficient was less than 0.3 for the group of metals Cr, Cu, Fe, and Mn. In the case of plants grown on non-treated fly ash experimental parcels, the translocation coefficient can reach values TC > 1.

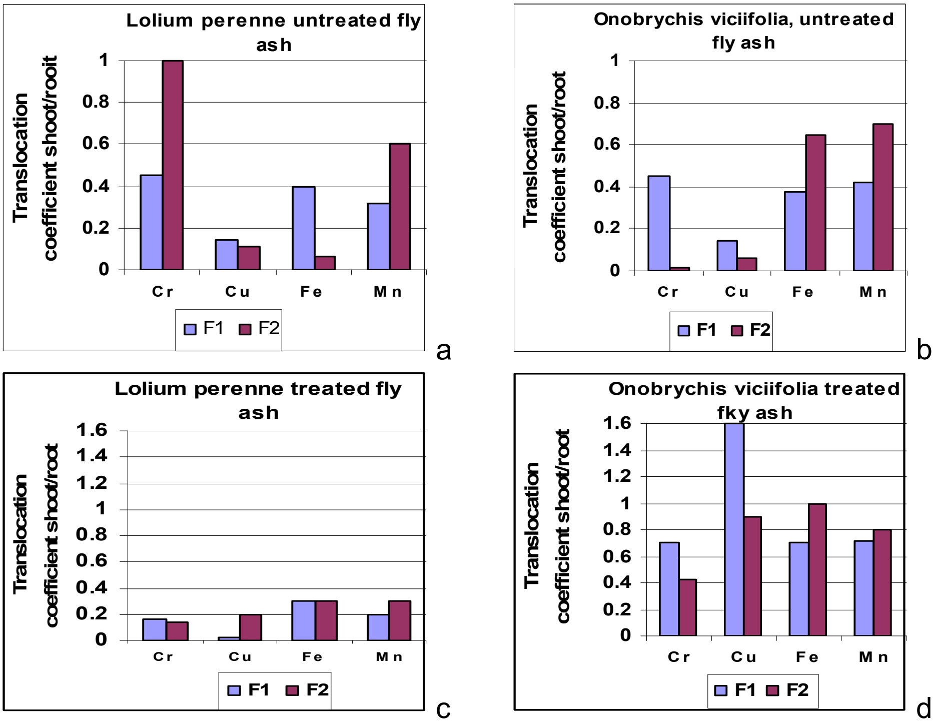

Figure 1. Cr, Cu, Fe, Mn , TC shoot/root: a) *Lolium spp.* non-treated fly ash, b) *Onobrychis spp.* non-treated fly ash, c) *Lolium spp.* fertilized fly ash, d) *Onobrychis spp.*fertilized fly ash. (F1-plants before harvest; F2-new cycle of plants).

For *Onobrychis viciifolia*, plants grown in non-fertilized topsoil of fly ash parcel, the TC was between 0.3 and 0.6. As can be seen, the addition of fertilizer may cause to some plant species the reducing of metal bioaccumulation in tissue, such as *Lolium perenne*, or increasing access of metals in the aerial part of plants as for the *Onobrychis viciifolia* species. For metals, such as Ni and Zn, biosolids addition alters the bioaccumulation in the aerial parts, especially in the phenophase of vegetative resumption in *Onobrychis spp.* species. *Onobrychis viciifolia* species accumulates in the aerial parts large quantities of these metals, in larger amounts than *Lolium perenne* species, in the same studied phenophases.

The TC for lead is greater in mature plants of *Lolium perenne* but is reduced below the detection to plants starting a new vegetative cycle. Addition of biosolids modifies metal access in plant tissue.

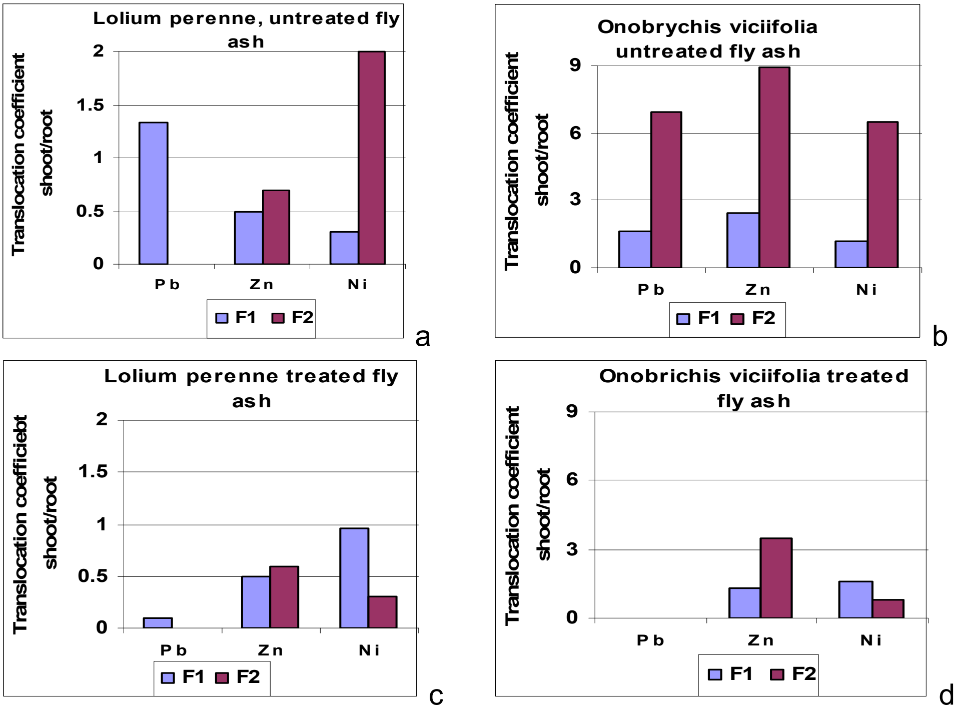

Figure 2. Pb, Zn, Ni translocation coefficient shoot/root: a) *Lolium spp.* non-treated fly ash, b) *Onobrychis spp.* non-treated fly ash, c*) Lolium spp.* fertilized fly ash, d) *Onobrychis spp.* fertilized fly ash; (F1-plants before harvest; F2-new cycle of plants).

CONCLUSIONS

Experimental studies based on to use of biosolids for fertilization of upper layers fly ash deposits (a waste lacking nutrients and resulting in burning lignite in power plants) led to the development of vegetation on these inert deposits. Pilot experiments confirmed a sustainable strategy for stabilizing/ phytoremediation of fly ash deposits, focused on capitalization of sludge waste, resulted in large amounts from municipal water treatment plants. The new crop installed presents characteristics depending on plant species: 1. Large biomass amount, but with accumulation of heavy metals, i.e. Cr, Cu, Ni, in the aerial parts of plants, such as in the case of leguminous *Onobrychis viciifolia* species, resulting vegetation with waste regime; 2. Lower biomass amount, with smaller accumulations of heavy metals, such as the case of grass *Lolium perenne,* with recycling possibilities in agro-zoo technical field (forage, bedding for animals, lignocelluloses support for compost). You can choose a path of rapid revegetation to restore the landscape with leguminous plants or a more slow vegetation of grasses, which can produce biomass without threatening the food chain.

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