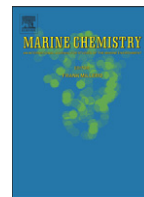




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Burial of agricultural byproducts in the deep sea as a form of carbon sequestration: A preliminary experiment

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ABSTRACT

Various methods that rely on new or undeveloped technologies, or that require large amounts of capital and energy, have been proposed for removal of CO₂ from the atmosphere. Of the methods that take advantage of the Earth's natural cycles, the approach of sequestering terrigenous agricultural byproducts in deep sea sediments has received little attention. To evaluate the potential of crop residue sequestration in deep sea sediments, a controlled 700 day incubation experiment was conducted where crop residues (soy stalk, maize stover, and alder wood chips) were added to deep sea hemipelagic sediments. An initial pulse of remineralization lasting 1 week oxidized less than 1% of the added material. Thereafter, remineralization rate constants for terrestrial materials (avg $k = 0.004 \text{ y}^{-1}$) were more than two orders of magnitude slower than for marine planktonic material incubated separately ($k = 3.0 \text{ y}^{-1}$). Over the 2-year incubation, soy residue was least remineralized (3%) with stover (6%) and wood (8%) also showing little remineralization compared to marine plankton (19%). Lignin losses were impacted by sediment redox condition, with the greatest degradation of lignin occurring under oxic conditions, but degradation of lignin continued under suboxic conditions for the maize treatment. Model fits to the data are consistent with the hypothesis that sequestration of terrestrial crop residues in the deep sea could effectively remove this material from the active carbon cycle. Implementation of crop residue ocean permanent sequestration (CROPS) could potentially remove as much as 15% of the current annual anthropogenic burden of CO₂ to the atmosphere. This idea, while unsavory, might represent a viable tool in the fight against the rise of atmospheric CO₂.

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1. Introduction

The effects of anthropogenically-sourced increases in atmospheric CO₂ are already being felt (IPCC, 2007) and numerous efforts are underway to evaluate or develop mitigation strategies (Pacala and Socolow, 2004; Strand and Benford, 2009; Wilson, 1992; Zeebe and Archer, 2005). Optimally, CO₂ mitigation should be quick, safe, repeatable, and inexpensive and any local impacts of sequestration offset by the greater good (Baker et al., 2007; IPCC, 2007). Virtually all the methods proposed to date for permanent carbon sequestration fail to meet these requirements (Strand and Benford, 2009). Of the methods that take advantage of the Earth's natural cycles, two have received testing; iron fertilization of the upper ocean (Zeebe and Archer, 2005) and sequestration in agricultural soils (Kimble et al., 2002; Post and Kwon, 2000). A third approach, sequestration of terrigenous agricultural byproducts in deep sea sediments (Metzger and Benford, 2001; Metzger et al., 2002), has received little attention despite natural analogues (Aller and Blair, 2004; Bianchi et al., 2007; Burdige, 2005; Burdige, 2007), and

reports that it may be more efficient and less expensive than other approaches (Metzger and Benford, 2001; Strand and Benford, 2009).

Strand and Benford (Strand and Benford, 2009) outlined the energetic merits of crop sequestration. Fully implemented, the burial of agricultural crops in the deep sea could potentially capture 15% of the current global CO₂ annual increase, moving carbon to sediments where it will ultimately be subducted or lignified. Crop sequestration uses existing capital infrastructure and technology (balers, barges, etc.) and is potentially much more energetically efficient than alternative uses of crop residues. They estimate that crop sequestration could be 92% efficient in sequestration of carbon while sequestration in soils is only 14% efficient and cellulosic ethanol production is only 32% efficient. Thus, based on potential energetic efficiency and ease of implementation, crop sequestration should be further investigated.

There are at least three reasons why crop sequestration receives little attention: a) large-scale implementation has the potential to be damaging to the marine environment, b) it seems odd to continue using fossil fuels for energy production while mitigating CO₂ rise by burying agricultural byproducts, and 3) putting bales of chaff in the deep sea seems 'too simplistic to make an impact'. While each of these criticisms requires further debate and evaluation, the complexities of

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the Anthropocene (Crutzen and Stoermer, 2000) demand that we explore all options. The emphasis in this manuscript is not to debate the relative merits of crop sequestration because the authors acknowledge that the idea is generally disagreeable, but to conduct the first systematic evaluation of the initial chemical stages of crop burial in the deep sea in case it becomes necessary. We focused on crop residue degradation in small mesocosms by modeling changes in carbon remineralization evaluated using oxygen micro electrodes, and by monitoring changes in the general compound class of hydrolysable amino acids and the crop-specific compound class of lignin phenols.

2. Materials and methods

Sediment was recovered from a water depth of 2625 m along the continental rise off Vancouver Island, British Columbia (48.34°N, 127.47°W) in August 2004 aboard the R/V Wecoma and sieved through a 500 µm mesh to remove large debris and large fauna. Soy stalk, maize stover, alder trunk and plankton (collected via plankton tow above the core location) were air dried (40 °C) until constant weight and then ground to pass a 256 µm mesh. Grinding the residues to a small size serves two purposes; it assures that each organic matter type is provided to the sediment with a similar surface area for heterotrophic microorganisms to attack the substrate, and it allows for uniform dispersion into the sediment cores. Carbon-equal amounts of each material, enough to raise the sediment organic carbon content by 2 wt.%, were individually homogenized into batches of the sediment. The sediment was then added to core barrels (6.35 cm diameter, 10 cm tall) that were sealed at the bottom, producing a 4 cm sediment layer. Quadruplicate treatments for control (no addition), plankton and each crop residue were added to a communal 50 cm deep incubation chamber filled with ambient deep seawater. The incubation chamber was placed in a 4 °C cold room and was kept continuously mixed and aerated. The carbon content of each sediment slurry was evaluated by elemental analysis.

Over a two year period, cores were periodically probed in 0.25 mm increments using an amperometric needle oxygen electrode (Diamond General) attached to a micromanipulator. The electrode was calibrated prior to each use. Dissolved O₂ concentration profiles for each core were used to calculate instantaneous sedimentary O₂ fluxes across the sediment–water interface using PROFILE software (Berg et al., 1998). For each sediment treatment, multiple measurements of instantaneous O₂ consumption were made ($n > 8$) and then averaged (after using PROFILE) for the replicate cores of each treatment. Results varied less than 12% between replicate cores and less than 5% within cores.

At the beginning of the experiment the cores were completely oxic, but suboxic and anoxic conditions developed rapidly at the bottoms of some cores. To assess overall carbon remineralization (oxic plus anoxic), we assumed that O₂ consumption due to reaction with reduced species other than carbon is ultimately driven by production of those species via carbon remineralization (Froelich et al., 1979) and thus oxygen consumption is an estimate of total (oxic + anoxic) carbon remineralization. A remineralization molar O₂:C ratio of 138:106 was used to convert O₂ fluxes to organic carbon remineralization rates (Redfield et al., 1963). Rates were then assumed to change linearly between time points over the 2-year period, and overall carbon remineralization for a given time period was determined by integration of the linear change in rate over time.

We acknowledge that burial of reduced species (e.g. iron sulfides) within anoxic portions of the cores represents a non-quantified component of carbon remineralization. This increases the quantity of carbon remineralized and make our data an underestimate of the actual carbon remineralization in the experiments. While a clear drawback to our experimental design, we argue that storage of reduced species such as iron sulfides is minimal in our system and unlikely to dramatically impact our results. This is based on visual observations and photographs

of cores in which we observe a continuous 'burn-down' of dark banding in the cores, replaced by rust colored bands. We interpret this as the oxidation of reduced iron resulting in iron oxide formation, a process which is captured by our oxygen data. The presence of iron sulfides in the anoxic layer thus represents the temporary storage of reduced species, storage which is ultimately captured in our quantifications as the oxygenated layer 'burns down' into the core. This is analogous to discussions and models developed for the Madeira Abyssal Plain turbidite sequences (Buckley and Cranston, 1988) and subsequent works.

The total amount of organic carbon remineralized prior to each sampling time point was subtracted from the total organic carbon content of the cores determined at the beginning of the experiment, yielding the amount of organic carbon remaining in the core at each sampling time. This data was then fit using a multi-G model containing a non-reactive component and at least one reactive component (Westrich and Berner, 1984). Data were modeled using the fewest reactive components needed to satisfy (99% tolerance) the statistic model offered by SigmaPlot 9.0. We report model output as degradation rate constants (per year) rather than remineralization rate constants in order to differentiate them from the original instantaneous remineralization rates derived from the O₂ microelectrode data recorded on a particular day of sampling. The control (no addition) and alder were best fit with a single degradable component, the maize and soy were best fit with two components and the plankton required three degradable components (Fig. 1; see also Section 3).

Over time cores were sacrificed for organic analyses. Twenty-five mm slices were obtained and weight percents of organic carbon and nitrogen were determined after vapor-phase acidification with a Carlo Erba model 1106 Elemental Analyzer (Hedges and Stern, 1984). Total hydrolysable amino acid (THAA) compositions were determined by HPLC using OPA derivatization (Cowie and Hedges, 1992; Keil and Kirchman, 1991). Lignin phenol analyses were analyzed by GC–MS after alkaline CuO oxidation in a microwave digestion system (CEM MARS) (Goni and Montgomery, 2000).

Maize stover and soy were selected because they comprise the two major angiosperm grass and shrub crops grown in the United States. Alder wood was selected as an alternative wood source because it is a perennial angiosperm tree, complementing the selection of the annual crops.

3. Results and discussion

The act of purposefully adding a pollutant to the deep ocean floor is generally unsettling, yet it is something that mankind has perpetrated

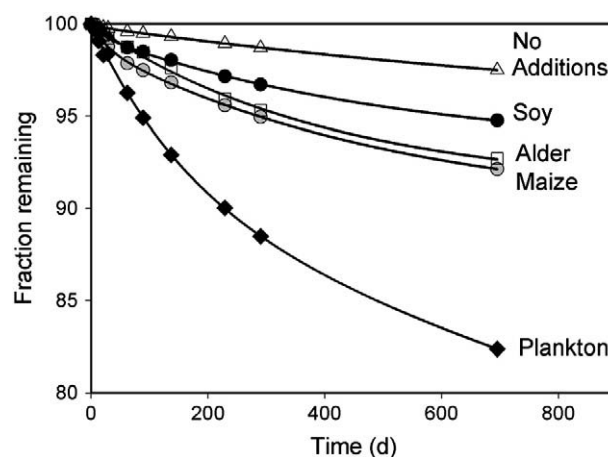


Fig. 1. Fraction of total organic carbon remaining over the extent of the incubation; control (triangle up), soy (circle), alder (square), maize (triangle down), and plankton (diamond).

for at least the last 150 years (Tyler, 2003). Currently, most purposeful dumping of waste material into the deep sea is illegal, as constrained by the London Convention (1972) and the USA's Ocean Dumping Ban (1991). These recent efforts to 'do the right thing' are laudable. However, in a time of great environmental change brought on by the aggregated actions of mankind (IPCC 2007), exploring options for mitigating the effects of our overall actions is necessary. This article attempts to set some initial conditions in case society is required to assess the possibility of mitigating a portion of atmospheric CO₂ rise by burying materials in the deep sea. Undoubtedly this act would alter deep sea habitat (Young and Richardson, 1998) and that aspect of sequestration needs to be developed further. In the present manuscript we evaluate the rate at which candidate crop residues survive chemical attack by microorganisms.

Multi-G model fits to the remineralization data have different numbers of reactive components depending on the substrate. This reflects gross differences in the reactivities of the organic matter mixtures being degraded. The marine plankton material has the most reactive components (three), and more than 44% of the material has a degradation rate constant greater than the fastest observed for the crop residues (e.g. k 's of 16.2 and 1.05 vs 0.06 y⁻¹ for soy; Table 1, Fig. 1). Degradation rate constants vary by more than four orders of magnitude between the least reactive material (control core with no organic matter addition, $k=0.008$ y⁻¹) and the most reactive material (marine plankton, $k=16.2$ y⁻¹; Table 1). Overall, the weight-averaged degradation rate constant for the agricultural crops (determined by combining all crop multi-g rate constants and weighting each by the corresponding fraction of organic matter with each rate) is 0.004 ± 0.0005 y⁻¹, which is more than two orders of magnitude slower than the weight-averaged value for the plankton (3.0 ± 0.1 y⁻¹). Similarly, the residual (non-reactive over a two-year time scale) component identified in the multi-g model fits is three times higher (90–93% nonreactive) relative to the plankton material (24% nonreactive). After 2 years, more than 92% of the crop residue remained (Fig. 1). Extending the model fits out to 100 years suggests that more than 75% of the crop residue will likely remain in the sediment (and indicate that the 'non-reactive' component is in fact slightly reactive). Thus, these incubation experiments indicate potentially large differences in the rate at which crop residues might be degraded in the deep sea relative to planktonic material, as well as in the quantity of material that will resist degradation. The results of these incubation experiments favor the further exploration of crop residue deep sea sequestration as a potential mechanism for removing carbon from the atmosphere and the active geological cycle.

If bales of crop residues were placed on the sea floor, one likely result would be the development of suboxic or anoxic waters within the bales. Our cores provide an analog for this effect because anoxic sediments developed at the bottoms of the sealed cores. Whether a difference in redox conditions influences organic matter remineralization is somewhat controversial (Calvert et al., 1992; Calvert and Pedersen, 1992; Hedges et al., 1999; Hedges and Keil, 1995), but is of

importance in the context of crop burial because sustained oxygen utilization within bales could ultimately lead to oxygen deficient patches of deep sea water around bales, leading to broad-scale impacts.

The possibility that oxygenation within the sediment is an important component limiting crop remineralization was evaluated using down-core changes in O₂ concentrations and the software PROFILE. Each sediment O₂ profile was modeled to determine oxygen consumption rates and then the oxygen consumption was converted to carbon remineralization. The flux across the sediment–water interface was assumed to represent total oxic + sub/anoxic oxygen demand, and the rate of oxygen consumption determined at the point in which oxygen concentrations approached zero was assigned as the 'suboxic and anoxic oxygen demand' (e.g. the downward flux of oxygen needed to neutralize the upwards flux of reduced species, for simplicity we will refer to this as the anoxic flux). Oxic respiration rates were then calculated by difference. Degradation rates under oxic and anoxic conditions were significantly different ($p < 0.001$; Table 2). Suboxic degradation rates are 1.33–3× slower than oxic rates, but they did not drop to zero over the 700-day duration of the experiment. This implies that anoxic conditions will not necessarily stop crop residue remineralization, but likely will slow it down.

The overall degradation rate constant (averaged for the oxic and suboxic regions and over the entire experiment) can be used to evaluate the gross-level impact of crop sequestration in the deep Gulf of Mexico, a potential location for such an activity due to its proximity to the Mississippi River and the grain belt of the USA. The necessary coverage of Gulf of Mexico deep sea sediment by crop material is estimated to be 0.02% of the total area of the deep Gulf of Mexico (Strand and Benford, 2009). We used deep water oxygen values of 225 μmol L⁻¹, a deep water volume of $\sim 2.5 \times 10^{17}$ L (Rivas et al., 2005) and an average degradation rate constant of 0.004 y⁻¹ applied to an estimated 0.15 Pg C crop residue available for sequestration (Strand and Benford, 2009) to estimate annual remineralization of crop residues back to CO₂. The calculation suggests that within the deep Gulf of Mexico, 6.5×10^4 mol of oxygen will be consumed per year, much less than 0.01% of the standing oxygen supply within the 0.02% of sea floor needed for crop sequestration. Thus, unlike the shallow shelf near the Mississippi River, which is impacted by seasonal low oxygen stress derived from nutrient inputs and plankton growth (Hazen et al., 2009), crop sequestration in the deep Gulf of Mexico would likely have a minimal impact on either the local or the overall oxygen budget of the region. In light of the recent BP oil spill in the Gulf of Mexico, any refinement of the idea of large-scale crop sequestration needs to evaluate whether the Gulf of Mexico is the correct location for such an activity.

Highly localized suboxia or anoxia within bales or within crop-laden sediments could play a key role in preserving lignin, and thus crop residues. Crop residues are rich in lignin, and the fungus and bacteria that degrade lignin typically use peroxidases to oxidatively cleave the random bonds within lignin. These enzymes are found only

Table 1

Multi-component multi-G model fits to cumulative degradation profiles for plankton, maize stover, soy stalk and alder wood. k is the rate constant (per year) and G is the percentage of total material with that rate constant. Subscripts: lab = labile component, int1 = intermediate lability component #1, int2 = intermediate lability component #2, and res = degradation resistant component. Model fits were optimized for fewer than four components when fewer components gave statistically similar results.

	k_{lab}	G_{lab}	k_{int1}	G_{int1}	k_{int2}	G_{int2}	G_{res}
Control					0.008	05.6	94.3
Plankton	16.2	11.8	1.05	33.1	0.041	31.0	24.1
Maize			0.04	1.2	0.002	09.1	89.7
Soy			0.06	0.6	0.002	06.4	93.0
Alder					0.003	08.8	91.1

Table 2

Average depth-integrated carbon degradation rates (μmol C cm⁻² d⁻¹) for oxygenated and anoxic components of sediment cores (averages of the data from days 62–700 of the experiment, $n=6$ sampling dates within that time interval), and average production rates for the nonprotein amino acids γ-amino butyric acid (γABA) and β-alanine (βALA) production rates (nmol C cm⁻² d⁻¹) for the uppermost sediment layer (0.25 cm) of each incubation type over the entire incubation (700 d).

	Oxic layer	Anoxic layer	Ratio O ₂ :SO ₄	γABA + βALA production rate
Control	0.4	0.2	2.0	$1.07^{-3} \pm 1.0^{-5}$
Plankton	1.9	0.6	3.1	$1.00^{-3} \pm 1.1^{-5}$
Maize	0.9	0.3	3.0	$1.12^{-3} \pm 1.2^{-5}$
Soy	0.4	0.2	2.0	$1.06^{-3} \pm 0.6^{-5}$
Alder	0.4	0.3	1.33	$1.11^{-3} \pm 1.2^{-5}$

in aerobic and fermentative species (Wong, 2009). Studies of lignin degradation are absent for the deep sea literature, but lignin degradation in shallow marine systems can be highly efficient, especially in the presence of oxygen and at higher temperatures (Benner et al., 1991; Dittmar and Lara, 2001; Louchouart et al., 1997; Miyajima et al., 1997). In our experiment, lignin loss during the incubation was impacted by sediment redox condition (Fig. 2). Similar to the bulk organic matter (Table 2), the greatest degradation of lignin occurred in association with exposure to oxygen, but degradation did continue under sub/anoxic conditions in the maize treatment (Fig. 2). Alder wood had the greatest initial lignin concentration and experienced the greatest absolute lignin loss (Fig. 2), but maize lost slightly more total organic matter during the incubation ($263 \mu\text{mol C cm}^{-2}$). Despite maize and soy having similar initial lignin concentrations, the maximum loss of maize-derived lignin was 4.5 times that of soy (Fig. 2). Overall, alder wood and maize stover underwent slightly greater total carbon remineralization than the soy (243 and 263 vs $175 \mu\text{mol C cm}^{-2}$, respectively).

The degradation of lignin using peroxidase enzymes has been shown to increase ratios of vanillic acid to vanillin (Ad:Al_v), and of syringic acid to syringaldehyde (Ad:Al_s), resulting from the oxidation of aldehyde side-chains (Hedges and Weliky, 1989; Louchouart et al., 1997). In the present study, increases in lignin acid content reflected changes in relative and absolute amounts of lignin phenols remaining in the incubation cores (Fig. 2 shows changes in Ad:Al_s). As the amount of lignin decreased, the ratio of acids to aldehydes increased, indicative of degradation. Thus, the lignin degradation within the experiment was detectable but was found to be minimal, similar to that observed for the bulk sediment organic matter in the treatments.

The impact of added crop residues on organic matter already present in the sediments was evaluated using amino acid biomarkers of organic matter 'degradation state' (Cowie and Hedges, 1994). Amino acids were a very small percentage of the added terrigenous material (<0.1%), but comprised 10% of the organic matter originally present in the sediment and 20% of the organic matter in the plankton added to the cores. Mole percentages of non-protein amino acids increased in relative concentration during degradation, and enrichment in these compounds is an indication of remineralization of proteins because they are by-products of the microbial degradation of common protein amino acids (Cowie and Hedges, 1994). Non-protein amino acid concentrations in the incubations increased at similar rates regardless of the additional inputs of the terrigenous materials (Table 2). This suggests that addition of crop residues to the sediments did not dramatically alter degradation rates for autochthonous organic material already in the sediment.

Burial of intact crop residues in the deep sea would most likely occur via the purposeful sinking of intact chaff, which would have a much lower surface area-to-volume ratio compared to the finely ground material we used in our experiment. Because our experiment was designed to evaluate the degradation of materials with a similar starting point, we were better able to evaluate the degradation phenomenon without the impact of changes in microbial or enzymatic access to the organic matter brought on by changes in material size and surface area (Keil et al., 1998). Our data show a two order of magnitude difference in degradation rates between the terrigenous crop residues and marine material. As an opening hypothesis, it is expected that if crop residues had been incubated in their natural form, degradation rates would have been even slower and the difference between terrigenous and marine materials amplified by inherent differences in material size. Thus, implementation of CROPS likely will result in retention of sequestered carbon that exceeds the sequestration estimates provided here.

While further research is clearly called for prior to wholesale deposition of crop residues in or on deep sea sediments, this method of carbon sequestration has several appealing attributes. First, it has natural analogs; the development of coal and gas fields eons ago, and river delta storm deposits now (Burdige, 2007). Second, the modern ocean currently assimilates and buries large amounts of terrigenous material (0.7 Pg C y^{-1}) delivered to coastal oceans by river systems (Hedges et al., 1997). Third, the infrastructure (balers to harvest residues, trucks to transport to rivers, barges to transport to sea, etc.) is already in hand and no new technology has to be developed to implement CROPS (Strand and Benford, 2009). Fourth, our back-of-the-envelope calculation suggests that the process will not create large 'dead zones'. Finally, crop sequestration in the deep sea is potentially more carbon-efficient in reducing atmospheric CO_2 (92%) than using the same materials either for soil sequestration (14%) or for cellulosic ethanol production (32%) (Strand and Benford, 2009). For these reasons, crop sequestration needs to be 'on the table' as we determine the best overall strategy for mitigating the rise of atmospheric CO_2 concentrations.

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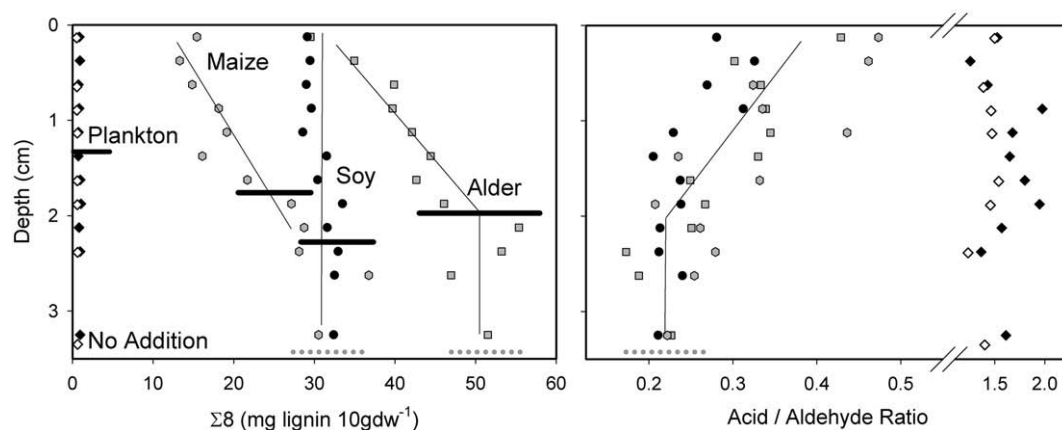


Fig. 2. Lignin yield (sum of the eight major phenols per 10 g dry sediment weight) and syringic acid/syringaldehyde ratios (Ad:Al) for the different incubations after 700 days incubation. Dotted lines near the bottom of the figures denote the starting values at the beginning of the incubation (± 1 std deviation). Solid lines in the first panel mark the extent of oxygen penetration into the cores after 700 days. Oxygen penetrated fully into the control core (no additions). Symbols as in Fig. 1.

conducted in this study; their comments improved the manuscript. This work was unfunded.

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