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Role of a Dense Bed of *Ophiothrix fragilis* (Abildgaard) in the Transfer of Heavy Metals at the Water–Sediment Interface

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The role of a dense bed of suspension-feeders (*Ophiothrix fragilis*) on the biogeochemical cycle of five major metals has been studied in the English Channel (Fe, Mn, Pb, Cu, Cd). Metal concentrations in ophiurids, their food (=suspended matter) and their faeces did not show any significant time variation. After their transit between food, organisms and faeces, metal concentrations were poorly modified, but relations between them changed. A lot of trace elements have been detected in the stomach, some of them typical of the waste inputs above the site. So, the ophiurid *O. fragilis* can be considered as a biological indicator of the elemental composition of the water mass entering the North Sea.

In the Dover Strait, the main factor which acts on the distribution of benthic communities is the strength of tidal currents. These reach their maximum in the narrower part of the Dover Strait (Anon., 1968). The sea floor off Cape Gris-Nez is comprised of flint pebbles whose size may exceed 10 cm and by a small amount of gravel and sand (Davoult *et al.*, 1988). This area is colonized by the sessile epifauna community; the ophiurid *Ophiothrix fragilis* is the dominant species in this community (Davoult, 1990). The demographic structure and the ecological characteristics of the population have been studied (Davoult *et al.*, 1990a,b; Gounin & Richard, 1992; Gounin, 1993). The spatial and temporal stability of this dense bed has been established; the mean density is about 1500 individuals (ind.) m^{-2} and the mean biomass (ash-free dry weight) is 210 g m^{-2} (Davoult, 1990). This biomass of *O. fragilis* is 62 ± 12% of the whole biomass of the community (Migné & Davoult, 1993). As *O. fragilis* is an efficient suspension feeder (Warner & Woodley, 1975), it allows an active transfer of particulate matter at the water–sediment interface in an area where hydrodynamic conditions are not favourable to a natural deposit of particulate matter.

The present study aims to determine if these organisms can accumulate particulate metals, and so partially decontaminate the near bottom water mass in an area where waste inputs are increasing (Chaussepied *et al.*, 1989), or if particulate metals only transit through the population; in this way, contaminants in the faeces would be altered and then scattered by tidal currents through pelagic compartment.

Materials and Methods

The study area is located about 3 nautical miles north-east off Cape Gris-Nez (50°55′N; 1°35′E). Samples were obtained with a Rallier du Baty dredge from the R/V *Sepia II*. The occurrence of pebbles made dredging the only possible method to sample ophiurids. Dates of sampling are indicated in Table 1.

Ophiurids were carefully rinsed on board ship and put in a plastic tank with 10 l of ambient seawater. Suspended matter was always >7% dry wt of the faeces collected. During the experiments, the density of ophiurids was always the same as the one observed *in situ* (200–400). Organisms were isolated from the bottom of the tank with a net to avoid any contact with their faeces. After 6 h of experimentation, three adults were dissected and ion microscopy was performed on sections of digestive epithelium previously fixed in

TABLE 1
Planning of sampling.

	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
O. fragilis in toto		×	×	×	×	×	×	×	×	×	×	×
Digestive epithelium			×	×	×		×		×	×	×	×
Faeces			××			×			×		××	
Suspended matter		×	×	×	×	×	×	×	×	×	×	×

Carnoy liquid. Other ophiurids were rinsed with Milli-Q water and stored at low temperature (≈ −20°C).

Faeces were collected after filtering the water of the tank through Whatman GF/C filters and rapidly frozen.

Seawater was sampled at the same station 1 m over the bottom with Niskin bottles. Suspensions were obtained after filtering the seawater through Whatman GF/C filters.

Sampling bottles (high-density polyethylene), filtration equipment (teflon ware, filters) were leached in HNO_3 (1 M) for several days and thoroughly rinsed several times with Milli-Q water prior to use. In addition, sample bottles were rinsed with seawater on site.

Flame atomic absorption spectrometry (Fe, Zn, Mn) or graphite furnace atomic absorption spectrometry (Pb, Cu, Cd; Laboratory of Analytical and Marine Chemistry of the University of Lille, France) was performed on suspensions, *in toto* ophiurids and faeces (Richard *et al.*, 1988).

Samples were oven dried at 110°C for 12 h, then weighed. They were mineralized by adjunction of HNO_3 65% (5 ml), HCl 32% (5 ml) and $HClO_4$ 70% (0.5 ml) (suprapur): a night at room temperature, then 4 h at 60°C.

Filters were then rinsed with 1 M HNO_3 and removed. Loss due to the shrinkage of the filter has been evaluated between 2 and 18% according to the metals (Zn was not analysed because of the high response of the reference filter). After evaporation, every deposit was diluted with 1 M HNO_3.

Mass spectrometry microanalysis (secondary ion microscopy) was performed to supply qualitative results at the cellular level (laboratory of Biophysics, Faculty of Medicine of Créteil). Samples of digestive epithelium were fixed in Carnoy liquid, dehydrated and embedded in paraffin wax. Thin sections (7 μm) were settled down on gold supports and dewaxed. The conditions of analysis were: primary ion beam (O_2^+): 500–800 nA; diaphragm of the emission lens: 200 μm.

Results

Mean annual variations of metals concentrations were picked up in three compartments: suspended matter, ophiurids and their faeces (Table 2). Results observed for suspended matter were between those noted in May and September during a tidal cycle at the same station (Table 3). Metallic concentrations in ophiurids were always below those observed in the suspended matter, except the Cd. The highest annual variability was noted for Fe, with maxima in April and May. Nevertheless, there was no significant difference between the extreme value and the annual mean. This result was the same for Zn (60 ± 6 μg g^{-1} dry wt); maxima for this contaminant were noted earlier, in February and March. Concentrations of metals in the faeces were generally higher than those in suspended matter; the annual variability was higher than the one observed in ophiurids (Table 2).

Factors of concentration in ophiurids were less than 1 for Fe, Mn and Cu (Table 2). For Cd, this ratio was always above 1 all the year; for Pb, it was close to 1, except in August (Fig.1). Factors of concentration in the

TABLE 3

Mean (± SD) metal concentrations (95% confidence limits) in suspended matter (SM) obtained during two tidal cycles in May (6 h) and September (2 h) (μg g^{-1} dry wt).

	SM	
Metal	May (n=13)	September (n=6)
Fe	5815 ± 2279	2144 ± 597
Mn	192 ± 52	73 ± 21
Pb	184 ± 149	31 ± 6
Cu	169 ± 71	26 ± 7
Cd	0.9 ± 0.1	1.9 ± 0.4

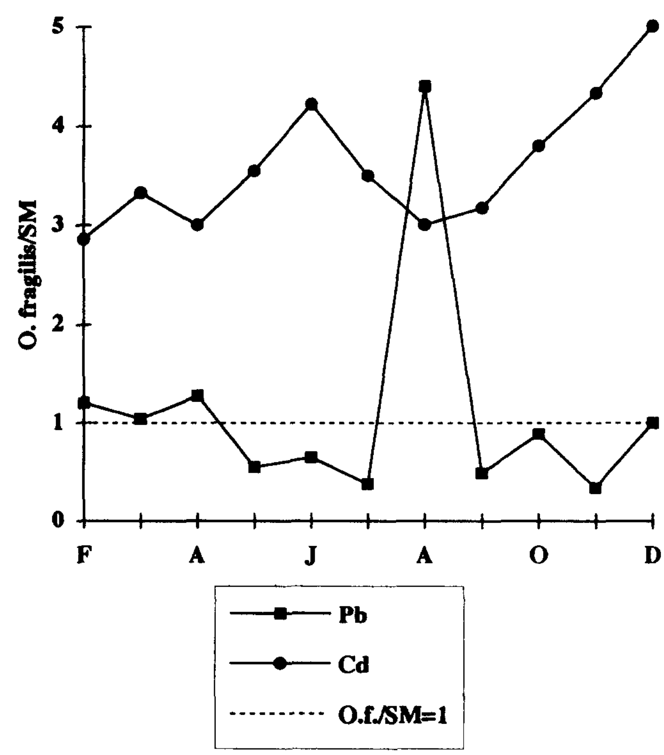

Fig. 1 *Ophiothrix fragilis* to suspended matter ratios (*O. fragilis*/SM) of Cd and Pb concentrations.

TABLE 2

Mean (± SD) annual metal concentrations (95% confidence limits) in suspended matter (SM), ophiurids and their faeces (μg g^{-1} dry wt).

Metal	SM (n=11)	*O. fragilis* (n=11)	Faeces (n=6)	*O. fragilis*/SM (n=11)	Faeces/SM (n=6)
Fe	4012 ± 1470	62 ± 11	5355 ± 1866	0.02 ± 0.01	0.94 ± 0.40
Mn	121 ± 23	39 ± 2	209 ± 94	0.34 ± 0.10	1.52 ± 0.79
Pb	35 ± 14	24 ± 1	164 ± 124	1.11 ± 0.77	4.40 ± 4.03
Cu	51 ± 20	4.2 ± 0.2	78 ± 37	0.11 ± 0.03	1.27 ± 1.27
Cd	1.1 ± 0.1	3.8 ± 0.1	1.9 ± 0.5	3.61 ± 0.45	1.77 ± 0.56

faeces were always above or close to 1 and showed a great annual variability (Fig. 2).

Significant correlations were detected between Fe and Mn ($p < 10\%$), Fe and Pb ($p < 10\%$), Pb and Cu ($p < 5\%$) in suspended matter. In the faeces, Fe was correlated with Mn ($p < 5\%$) and Mn was anti-correlated with Cd ($p < 5\%$). A principal components analysis (centred values) was performed on correlations between heavy metals (=variables) within the three compartments (=observations). Axe 1 (Fig. 3(a)) is determined by the variables Fe–Mn, Mn–Cu, Pb–Cu and Mn–Pb (=71.5% of the total contribution): the relation between these metals was positive in suspended matter and faeces and negative in ophiurids. The relation was negative in suspended matter and faeces and positive in ophiurids for the variables Cu–Cd, Pb–Cd and Fe–Cd. No tendency could be detected for correlations Mn–Cd, Fe–Cu and Fe–Pb. Correlations between metals appeared to be opposed in ophiurids on one hand and in suspended matter and faeces on the other hand (Fig. 3(b)).

Significant differences occurred for Fe ($p < 5\%$) and Mn ($p < 0.1\%$) between young (disc diameter ≤ 4 mm) and adult (disc diameter ≥ 8 mm) ophiurids (Figs 4 and 5). Zn was always higher in adults; seasonal evolution of Pb, Cu and Cd was quite similar between young and adults.

Ion microscopy detected several trace elements in digestive epithelium of ophiurids. The most abundant among those not detected in atomic absorption spectrometry are listed in Table 4. Indium, tin,

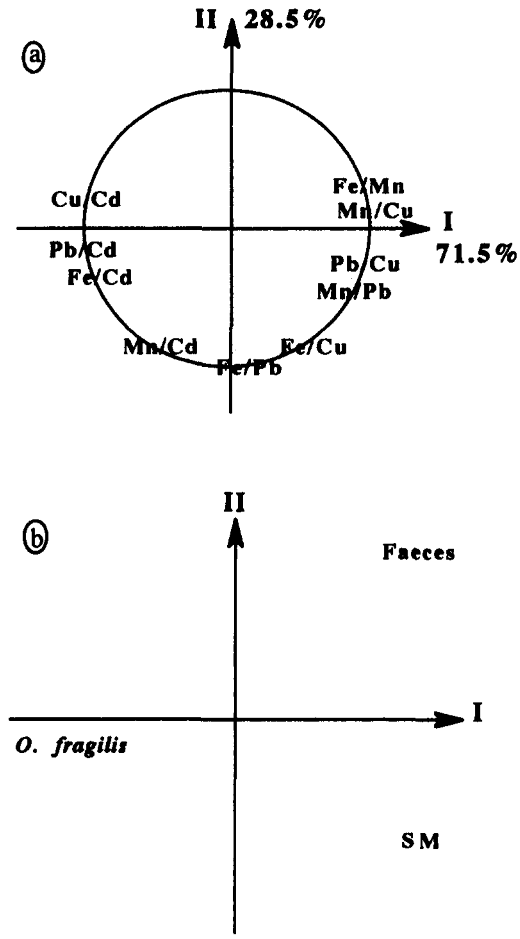

Fig. 3 Plot of variables on axes I and II of the PCA realized on correlations between heavy metals in suspended matter, ophiurids and faeces (a); Plot of individuals (suspended matter, ophiurids and faeces) on axes I and II of the principal components analysis (b).

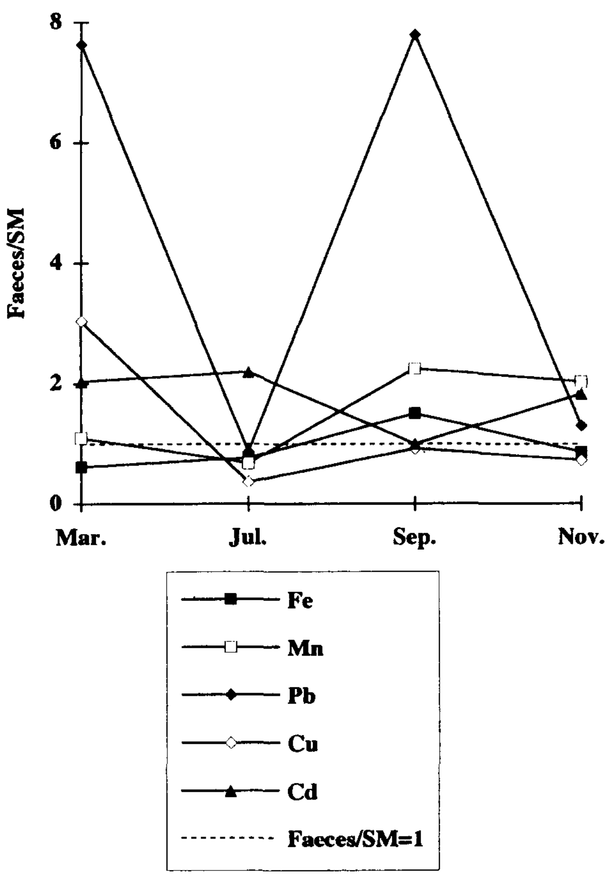

Fig. 2 Faeces to suspended matter ratios (faeces/SM) of Fe, Mn, Pb, Cu and Cd concentrations.

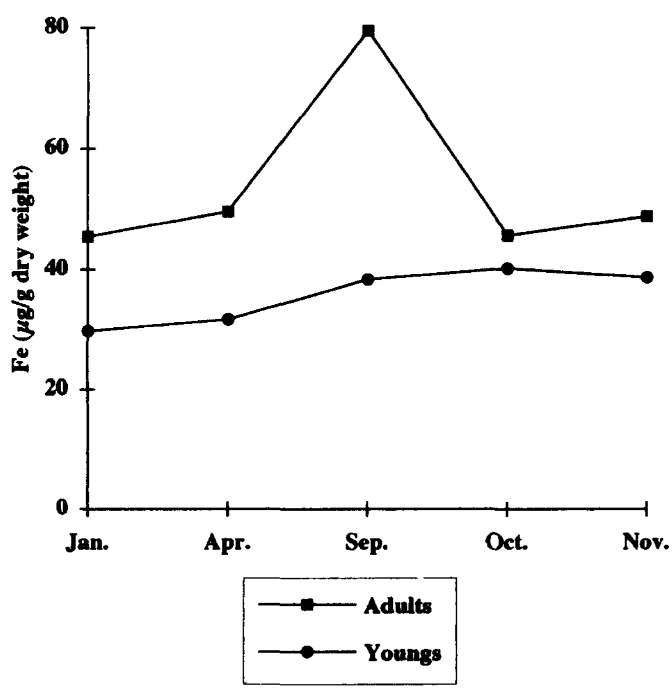

Fig. 4 Fe concentrations in young and adult ophiurids.

TABLE 4
Ion microscopy: results obtained from different zones of the digestive epithelium.*

Date	Digestive zone	$^{7}Li^{+}$	$^{107}Ag^{+}$	$^{138}Ba^{+}$	$^{139}La^{+}$	$^{169}Tm^{+}$	$^{209}Bi^{+}$	$^{238}U^{+}$	$^{239}Pu^{+}$
March	·Interradial p.	+	++	+	LD	LD	LD	LD	LD
April	Interradial p.	tr	++	+	tr	LD	LD	tr	tr
May	V. roof	+	+	+	tr	LD	LD	tr	tr
	Interradial p.	+	++	+++	tr	tr	LD	tr	tr
	V. floor	+	+	++	tr	LD	LD	tr	tr
July	V. roof	+	+	+	tr	tr	LD	LD	LD
	Interradial p.	tr	tr	+	LD	LD	LD	tr	tr
	V. floor	+	+	++	tr	LD	LD	LD	LD
September	V. roof	tr	+	tr	LD	LD	LD	LD	LD
	Interradial p.	+	+	tr	LD	LD	tr	LD	tr
	V. floor	+	+	tr	LD	LD	LD	tr	tr
October	Interradial p.	++	++	+	tr	tr	LD	tr	tr
November	Interradial p.	tr	+	++	tr	tr	LD	LD	LD
December	Interradial p.	tr	++	++	tr	tr	LD	LD	LD

*p, Pouch; V, vestibular. For every element, the major isotope is given. Ion emission intensities: DL, detection limit; tr, trace; +, 10^{-16}; ++, 10^{-15}; +++, 10^{-14}.

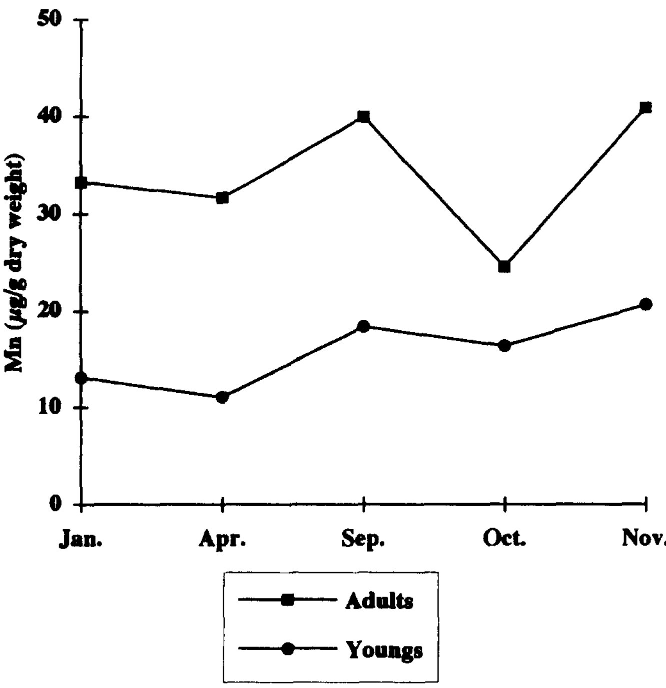

Fig. 5 Mn concentrations in young and adult ophiurids.

antimony, tellium and cerium have been detected too. No difference in contamination between the digestive zones could be detected.

Discussion

Heavy metals present in coastal waters (Richard *et al.*, 1988) were detected in *O. fragilis* in the same order of concentrations:

$$Fe > Zn > Mn > Pb > Cu > Cd.$$

Young ophiurids were quickly contaminated; Pb, Cd and Cu were detected at the same level in young and adults. This can be explained by the same diet of young and adults (pers. comm., Jangoux).

Factors of concentration for Fe, Mn, Pb and Cu were less or close to 1: there was no bioaccumulation from lower level (suspended matter) to upper level (ophiurids) of the trophic chain. Assimilation rate of these metals by digestive way was low, as usually shown in marine organisms (Bouquegneau *et al.*, 1992). Factors of concentration below 1 for Fe, Mn, Pb and Cu have been detected for another suspension feeder (the mussel, *Mytilus edulis*) sampled on the Belgian coast (Bouquegneau *et al.*, 1992).

On the contrary, the ratio for Cd was higher, whatever the season. Delabre (1985) reported that higher metal concentrations in marine organisms than *in situ* could be due to the incorporation of these contaminants by dissolved way. An experimental contamination of ophiurids with $CdCl_2$ (the most important form in seawater, Flament *et al.*, 1985) showed that contamination by dissolved Cd was possible in these organisms (Gounin, 1993). This way of contamination could contribute to increase the accumulation of this metal by alimentary canal in *O. fragilis.* The influence of the metallic contamination by dissolved way was detected for vanadium (Miramand *et al.*, 1982) and plutonium (Guary *et al.*, 1982) in other echinoderms. High values in Cd occurred in *Alcyonium digitatum* (3.5 ± 0.2 µg g^{-1} dry wt) and in hydroids too (2.5 ± 0.1 µg g^{-1} dry wt), two other suspension feeders sampled in the area (Davoult, unpublished). This high contamination of Cd in these organisms could indicate an important contamination by dissolved way (≈ 58 ng l^{-1} in surface water in the area, Flament *et al.*, 1985); this could partly explain that young individuals are rapidly contaminated by this metal. Delabre (1985) reported that Cd is the contaminant the most released under dissolved way from dumping dredge spoils which are one of the most important source of metallic contamination in the area.

A lot of metals have been detected in the digestive epithelium of *O. fragilis*; some of them are not typical of the waste inputs in the area (Chaussepied *et al.*, 1989). Lithium (Li) and barium (Ba) are always detected in marine organisms (Chassard-Bouchaud *et al.*, 1984, 1985), independently of any biotope or geographic area. Silver (Ag) was one of the most abundant contaminant in the stomach; according to Guegueniat (1986), Ag has been detected in the suspensions of the Seine and the Orne, but not in other great French rivers. Ag is very toxic for marine organisms because of its high biodisponibility from sediments. Lanthanum (La) is also considered as a specific tracer of the inputs of the Seine (Guegueniat *et al.*, 1986). La and thulium (Tm) were detected in the digestive epithelium of *O. fragilis*; these rare earth elements are present in phosphogypsum which are released in great quantity into the Bay of Seine. La and Tm have been detected in the digestive epithelium (Gounin, 1986) and the gonads (Chassard-Bouchaud *et al.*, 1988) of *O. fragilis* sampled in the Bay of Seine. Uranium (U) and plutonium (Pu) were also present in *M. edulis* in this area (Chassard-Bouchaud *et al.*, 1986; Calmet *et al.*, 1987). These contaminants are present in the French part of the Dover Strait. Suspensions are carried by the residual tidal current from the western English Channel towards the Dover Strait: waters accumulate in the English Channel the contaminants released above this area. It is not surprising to find them in the digestive tract of the ophiurid which incorporates the chemical characteristics of the water flux near the bottom. A previous study indicated that La and Tm were not significantly detected in the digestive epithelium of the species sampled off Roscoff (Gounin, 1986), an area which is not submitted to the inputs of the bay of Seine.

In the area, the variability of the inputs of particulate metals is high, according to tidal and seasonal scales, but it did not show any cyclic evolution (Gounin, 1993): only few fluctuations were detected in the annual evolution of the metallic concentrations in *O. fragilis*. Meanwhile, bioaccumulations in the stomach and the gonads of the species sampled in the Bay of Seine seem to be under seasonal cycle (Chassard-Bouchaud *et al.*, 1988); this is probably a consequence of the proximity of the estuary of the Seine where inputs of contaminants vary in relation with the seasonal cycle (Avoine, 1986).

In a previous study (Gounin, 1993), it was shown that Fe and Mn were both correlated with organic matter in suspended matter; Pb, Cu and Cd vary in a different way. This could explain the high concentrations in Fe and Mn noted in adult ophiurids who need more nutrients than young. Moreover, the principal components analysis showed that Mn and Cd vary in a different way. The correlation between these two metals was always negative; this indicates that these contaminants are not abundant in the same time within the three compartments. This can be explained by the higher concentration of dissolved Cd (Flament *et al.*, 1985) than of dissolved Mn (Skiker *et al.*, 1988) in the area.

This ecotoxicological approach allowed us to conclude that *O. fragilis* does not accumulate metallic contaminants which only transit through the 'ophiurid' compartment. Nevertheless, metals are not simultaneously abundant in the 'food', 'ophiurid' and 'faeces' compartments; this modification of the relations between them may result from the action of digestive processes on the bolus. These qualitative modifications may induce modifications in biodisponibility of heavy metals for deposit feeders in the area. Meanwhile, this action would be limited because of the strength of tidal currents in the area. When tidal currents increase, a partial redistribution of the biodeposit from the bottom to the water mass occurs, that is favoured by the rapid desegregation of the not well-consolidated faeces (Gounin, 1993).

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