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CONSIDERATIONS REGARDING TRACE METAL PRESENCE IN MARINE ECOSYSTEM COMPONENTS ALONG THE ROMANIAN BLACK SEA COASTAL ZONE

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ABSTRACT

Romanian Black Sea coastal marine area is influenced by anthropogenic pressures induced by fluvial inputs and coastal economic activities. Most metals are naturally occurring components of the marine environment, but anthropogenic inputs could lead to increased levels in coastal zones. Trace metals tend to accumulate along the food webs, with possible negative consequences on marine organisms and, ultimately, on human consumers.

The paper is based on the results of the monitoring of copper, cadmium, lead and manganese levels in seawater, sediments and biota, along the Romanian shore between Sulina and Vama Veche. The variation range, spatial distribution as well as the determining factors on trace metal dynamics along the Romanian Black Sea coast are presented.

This overall assessment concerning the state of pollution with trace metals contribute to the characterisation of the quality status of the marine environment, identifying the areas where anthropogenic impact is noticeable.

KEY WORDS : trace metals, pollution monitoring, Black Sea

INTRODUCTION

Romanian marine coastal area is under a constant anthropogenic pressure: the northern sector (Sulina – Gura Buhaz) is strongly influenced by the Danube pollutant load, whereas in the southern sector (Mamaia Bay – Vama Veche) pollution sources are represented by urban and industrial waste water discharges, harbour activities, navigation, tourism, etc (MIHNEA, PECHEANU, 1984; PIESCU *et al.*, 1997).

Pollutants have multiple pathways of entering, accumulation and transport in marine ecosystems and this lead to the difficulty of identifying the contribution of each specific source. Toxic contaminants from seawater are often bound to the particulate suspended matter, being gradually accumulated in sediments. Here, they are subject of complex interactions, and they could be imobilised, resuspended or uptaken by the marine organisms (RILEY & SKIRROW, 1975).

Most metals are naturally occurring components of the marine environment, but anthropogenic inputs (waste waters, industrial activities, mining, energy production, products manufacturing, etc) lead to increased trace metals levels in coastal zones (ALZIEU, 1999). Trace metals tend to accumulate along the food webs, with negative consequences on marine organisms and, ultimately, on human consumers.

MATERIAL AND METHOD

During 2002 seawater and surface sediments have been sampled from the monitoring stations between Sulina – Vama Veche, along the 0, 5 and 20 m isobaths; reference station East Constanta (20 and 60 m isobaths) has also been included. Seawater and sediments sampling was carried out monthly, using bathometers and a Van Veen bodengreifer, respectively. Before trace metals analysis, seawater samples were preserved in plastic bottles and acidified with ultrapur nitric acid (1-5 ml HNO_3/1 l seawater). Each sediment sample was oven dried at 120^0C, homogenized, weighed and digested with concentrated nitric acid (IAEA, 1995).

Marine biota samples were also collected and analysed for trace metals: mussels (*Mytilus galloprovinciali)* and some economically important marine fish species, like anchovy, whiting, bluefish, horse mackerel, spratt, goby and turbot. Sampling was performed using fisherman's nets along the coastal zone and also by trawling using "Steaua de Mare" research vessel.

Fish samples were placed in plastic bags, transported to the laboratory and stored at below -20^0C until analysis. Each sample usually consisted of at least ten individuals selected from the catch. Each fish was then dissected and edible part (muscle) has been separated and further analysed for trace metals.

Mussels samples belonging to the class of length 4.5-5 cm have been selected (ten individuals from each location) and analyses were carried out on whole specimens, excluding shells. The soft parts of the shellfish were removed from the shells, washed in seawater, quickly rinsed in bidistilled water.

Biota samples were then homogenized weighed and digested with concentrated HNO_3 (IAEA, 1993). For sediment and biota samples digestion, closed Teflon vessels and a hot plate with thermostatic control have been used. After digestion wet digested samples were cooled and diluted to 100 ml with bidistilled water.

All samples were analyzed for trace metals (Cu, Cd, Pb, Mn) on an ATI-UNICAM 939Z graphite furnace atomic absorption spectrometer (GF-AAS), with Zeeman background correction device.

RESULTS AND DISCUSSION

Seawater

Average trace metal concentrations in seawater samples along the coastal zone, observed in 2002, varied between the following limits: copper 0.27 – 17.39 μg/l, cadmium 0.089 – 1.88 μg/l, lead 1.19-21.95 μg/l, and manganese 1.17 – 50.92 μg/l. As depicted in fig. 1, 2, 3, average trace metal concentrations followed an irregular distribution pattern along the coastal zone. Considering as reference open sea waters (East Constantza profile) where trace metals were detected in extremely low levels, higher concentrations were observed especially in northern sector at Danube mouths and also in southern sector, in specific locations influenced by waste waters discharges, harbour activities, etc.

Shore seawater samples (0 m isobath) had slightly higher **copper** concentrations in Mamaya Bay and Mangalia stations: 16.99 μg/l and 10.55 μg/l, respectively. Along the 5 m isobath could be evinced Constantza South (10.93 μg/l copper) and Eforie South (8.82 μg/l copper). In the case of 20 m depth samples, maximum copper concentration was observed in Portita location (17.39 μg/l). Open seawater (60 m isobath) was characterized by moderate copper levels (3.28 μg/l), about 2.5 lower than medium value for shallow waters area, between 0 and 20 m depth.

Cadmium had much the same distribution observed for copper: very low concentrations in shore seawater (0.29 μg/l) and, along the 5 m isobath, increased levels in the locations affected by waste water discharges – Eforie South (1.76μg/l) and Constantza South (1.45 μg/l). Along the 20 m isobath, maximum concentration was registered in Portita (1.88 μg/l), whereas the lowest level appeared in reference station Est Constanta (0.13 μg/l).

The highest **lead** concentrations were noticed in the following areas: Mangalia (shore seawater) - 21.95 μg/l, Mamaya Bay (5 m isobath) - 6.4 μg/l, and also in Sulina (20 m isobath) – 5.67 μg/l. Open sea waters (60 m depth) were again characterized by lower levels – about 4 times smaller than coastal waters average value.

Manganese concentrations had a tendency to decrease along with increasing of the water depth: from a medium value of 26.35 μg/l between 0 and 5 m isobath, to 12,3 μg/l along the 20 m isobath; manganese reached extremely low concentrations in open sea area (60 m depth) – 4,76 μg/l.

The average trace metals concentrations registered in 2002 in coastal waters were situated below the limits stipulated by national regulations.

Sediments

Increased levels of suspended particulate matter from coastal areas facilitate the removal of dissolved trace metals from seawater, through adsorbtion, and further these particles sink down gradually, being accumulated in sediments. Thus, marine sediments play a key role as a site for contaminants accumulation in coastal areas influenced by industrial and urban activities. The investigations carried out on surface sediments resulted in relevant informations about the state of quality of the marine environment.

Copper concentrations in sediments samples analysed in 2002 varied between 15.81 – 183.48 μg/g dry weight (Fig. 1, 2, 3). Considering the moderate values from open sea area (60 m) – 34.59 μg/g d.w. copper, coastal sediments were defined by significantly higher levels: 69,2 μg/g d.w. average value along 5 m isobath and respectively 61,07 μg/g d.w. along 20 m isobath. The strong anthropogenic impact (sewage outfalls) is reflected in sediments from Constantza South (183.48 μg/g d.w.), Mangalia (90.87 μg/g d.w.), Eforie South (80.27 μg/g d.w.) and also, in northern sector, fluvial input is responsible for higher copper concentration in Portita sediments (95.43 μg/g d.w.).

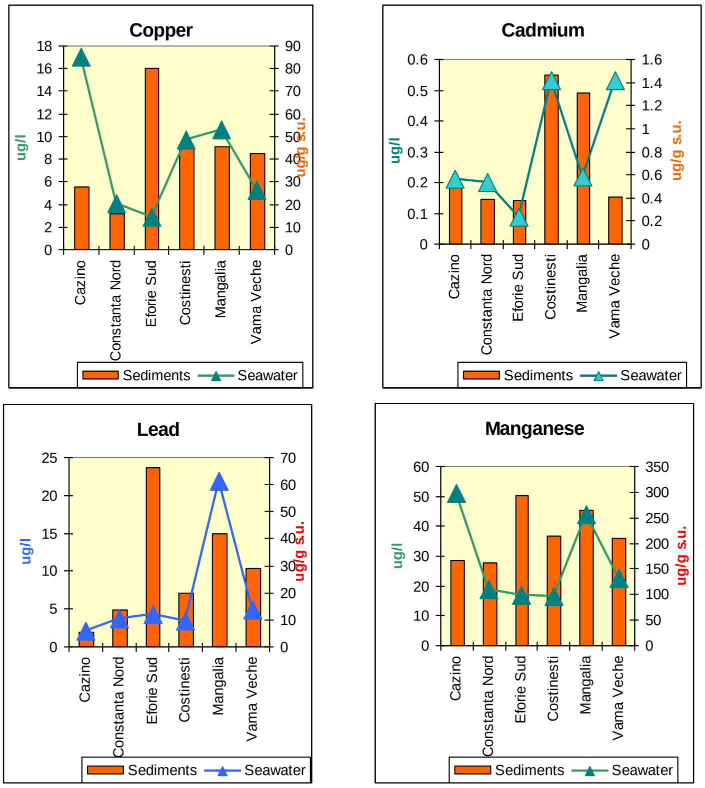

Fig. 1 - Trace metal levels (copper, cadmium, lead and manganese) in seawater and sediments samples in the shore area (0 m isobath)

In the case of **cadmium**, along the Romanian littoral, concentrations between 0.38 – 19.92 μg/g d.w. were registered (Fig. 1, 2, 3). Uncontaminated marine sediments presented quite lower cadmium content: 0.9 μg/g d.w. in reference station East Constantza (20 m) and 0.66 μg/g d.w. average value for open sea area (60 m depth). On the contrary, sediments from the northern sector, strongly influenced by the fluvial input, had an average level 14 times higher than reference station East Constantza. The same situation was observed in the southern coastal zone, where average cadmium levels along the 5 m isobath were 12 times higher than reference values and, respectively, along the 20 m isobath, 9 times higher than refence values. Shore sediments were characterized by rather lower cadmium concentrations – medium value for Cazino – Vama Veche sector being 0.74 μg/g d.w.

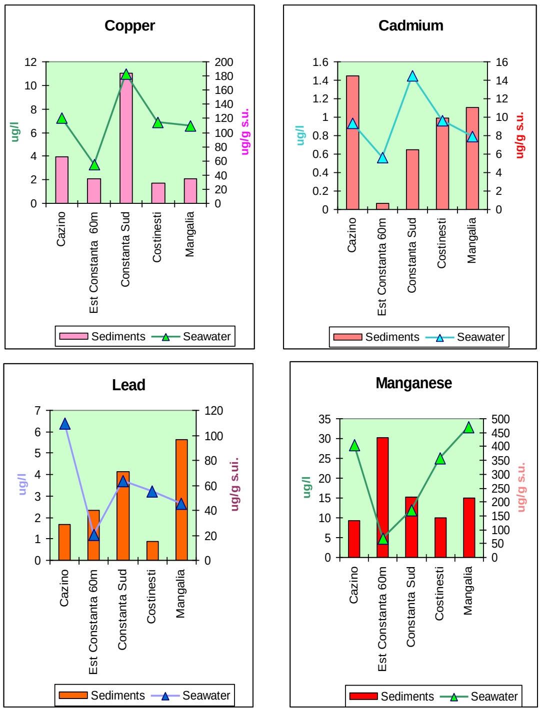

Fig. 2 - Trace metal levels (copper, cadmium, lead and manganese) in seawater and sediments samples along 5 m isobath, comparing with open sea area (60 m depth)

Lead content in the surface sediments varied in 2002 between the limits 5.26 – 96.89 µg/g d.w. (Fig. 1, 2, 3). In the southern sector, within 0 and 20 m isobaths, waster discharge influences are reflected in the higher lead concentrations in the sediments from Constantza South, Eforie South and Mangalia, comparing with open sea area (60 m depth) where a medium value of 39.77 µg/g d.w. was noticed. Also, sediments from Sulina – Chituc sector, under the fluvial influence, were defined by significantly increased lead concentrations, 2 times higher than uncontaminated sediments from deep sea area (60 m isobath).

Mangenese content in sediments varied between 134.3-521.08 µg/g d.w. (Fig. 1, 2, 3). The highest levels were noticed in northern sector (20 m depth) (average value 452.17 µg/g d.w.), and also in the open sea area (60 m depth) – 433.26 µg/g d.w., due to their granulometric characteristics.

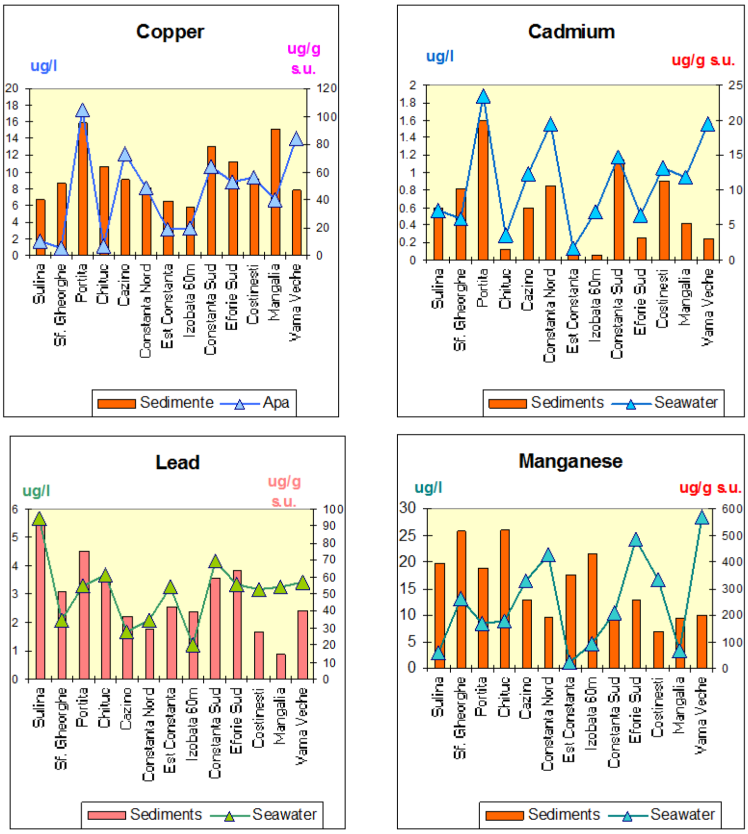

Fig. 3 - Trace metal levels (copper, cadmium, lead and manganese) in seawater and sediments samples along 20 m isobath, comparing with open sea area (60 m depth)

Trace metals dissolved in seawater have a high affinity for fine suspensions, like iron and manganese oxyhidroxydes, which are transported and deposited in the open sea area. For this reason, contaminants and especially trace metals, are associated with the fine-grained fraction of marine sediments (clays, silts), coarser material (sand), with a lower affinity, acting as a diluent of the total concentration (LORING, 1991). Thus, the majority of shore sediments investigated in 2002 had in generally lower trace metals levels than the others.

The investigations carried out in 2002 demonstrated that trace metals levels in marine sediments along the Romanian marine coastal zone show much variation, depending, first of all, of anthropogenic impact (waste water discharges, fluvial input, etc), grain-size features and variability of the physico-chemical and hydrodynamic conditions in the marine environment.

Average trace metal levels observed in 2002 in marine sediments don't display a significantly higher pollution degree of the coastal zone and, moreover, these values have a slightly decreasing tendency comparing with previous years of investigations.

Marine organisms

Some metals, like iron, copper, manganese, cobalt, zinc, are essential for all living organisms, being vital components of many enzymatic systems, but even these elements could become toxic in higher quantities. Others, like cadmium, lead, mercury, arsenic, are highly dangerous, even in very low levels (DEPLEDGE & RAINBOW, 1990).

Marine organisms play an important role in trace metal biogeochemical cycles in marine environment. Among the factors that influence bioaccumulation, trace metal concentrations and also their chemical form (speciation) in the marine environment are the most important.

Metals ions absorbtion from seawater may occur across the general body surface, or through special areas like gills or intestinal walls. Absorbtion from food and ingested particles at digestive tract level represent also an important source of metals for marine organisms (BRYAN, 1971).

Trace metals bioaccumulation levels in mussels - *Mytilus galloprovincialis*

Mussels, sessile and filtering organisms, are recognized and widely used as pollution bioindicators for many contaminants, reflecting the contamination degree of the marine environment.

During 2002, mussels samples from Portita, Constantza North, Agigea, Eforie South, Costinesti and Mangalia have been investigated for trace metals, along with seawater and sediments samples.

Cadmium bioaccumulation levels were rather moderate, varying between 0.087-0.82 μg/g wet weight (average value 0.46 μg/g w.w.) (Fig. 4). Increased tissular levels for cadmium have been found in mussels from Portita, Constantza North and Costinesti, locations characterized by higher cadmium concentrations in seawater and sediments also (Fig. 3). Considering the results from previous year of monitoring, in 2002 cadmium bioaccumulation in mussels presented a decreasing tendency.

Another toxic element, **lead**, appeared in low quantities in mussels samples investigated in 2002, even below analytical limit in two cases: Agigea si Eforie Sud. Lead concentrations were between 0.005-0.32 μg/g w.w., with an average value of 0.11 μg/g w.w.) (Fig. 4). Maximum value was noticed in Constantza North location (sewage outfall). Similar with cadmium, lead concentrations were smaller in 2002 comparing with previous year

Copper, essential element, but toxic beyond certain limits, was found in concentrations between 1.49 – 4.69 µg/g w.w. (medium value 3.26 µg/g w.w.). Again, mussels from the following locations: Portita, Constantza North and Costinesti were evinced as having the highest bioaccumulation levels (Fig. 4). The minimum concentration (1.49 µg/g w.w.) has been registered in Eforie South. No significantly differences with the results of previous year of investigations have been noticed.

For **manganese**, another essential element, concentrations of 1.41-5.46 µg/g w.w. (average value 2.92 µg/g w.w.) were observed (Fig. 4). Again samples from Constantza North and Costinesti presented the highest values, and from Eforie South the smallest. Considering previous year, in 2002 manganese concentrations are slighlty increased.

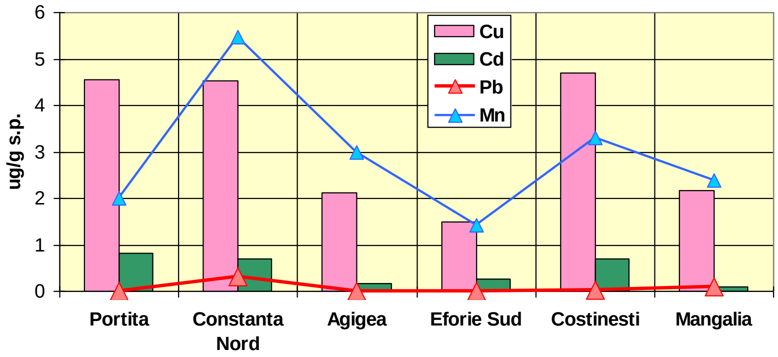

Fig. 4. Average trace metal bioaccumulation levels in mussels along the Romanian littoral in 2002

Trace metals bioaccumulation levels in some marine fish species

During 2002, edible tissue (muscle) samples from some economically important marine fish species have been investigated for trace metals, as follow: anchovy, whiting, bluefish, horse mackerel, spratt, goby and turbot. Fish were captured from the following areas: Vadu, Midia, Mamaia Bay, Constantza North, Eforie South and Mangalia. Average trace metal tissular levels, registered for these marine fish, were generally (maybe with the exception of lead) lower than those observed in mussels samples.

Cadmium presented concentrations between 0.06-0.59 µg/g w.w. (average value 0.28 µg/g w.w.) (Fig.5.). Maximum accumulation was noticed for small pelagic planktivorous fish - anchovy (caught from Vadu location) and sprat (Mamaia Bay), whereas the lowest cadmium concentrations appeared in predators fish - bluefish (0.084 µg/g w.w.) and horse mackerel (0.06 µg/g w.w.), both captured from Midia location. Cadmium content in analysed samples, excluding bluefish and horse mackerel, was slightly above maximum admisible limit for cadmium in fish products (0.1 µg/g w.w.), according to national regulations (OMS 975/1998).

In the case of **lead**, concentrations between 0.022-3.68 µg/g w.w. (medium value 0.98 µg/g w.w.) were observed. Increased levels, beyond maximum admisible limit for fish products (0.5 µg/g w.w), have been evinced in whiting, anchovy and sprat (Fig.5). Similarly with cadmium situation, predator fishes (bluefish and horsemackerel) were characterized by extremely low lead concentrations in their tissues.

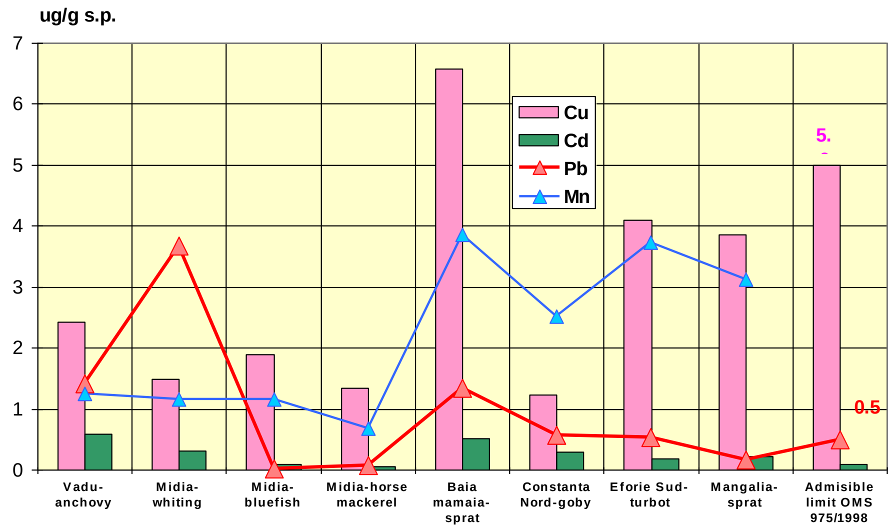

Fig. 5. Trace metals bioaccumulation levels in marine fish species along the Romanian littoral in 2002

Copper concentrations were between 1.24-6.57 µg/g w.w (average value 2.86 µg/g w.w.) (Fig. 5). Only sprat samples from Mamaia Bay displayed an increased copper level, slightly higher than maximum admisible limit (5.0 µg/g w.w.). Turbot samples from Eforie South presented also higher copper concentrations, but without surpassing the limits.

Manganese was found in concentrations between 0.68-3.86 µg/g w.w. (average value 2.18 µg/ w.w.) (Fig. 5). Higher concentrations were again evinced in sprat samples, and also in benthic fish (goby, turbot), whereas the minimum value was registered for horse mackerel.

Comparing the results obtained in 2002 with previous year of investigations, it could be notice that cadmium, lead and copper concentrations in marine fish edible tissue had a clear tendency of decreasing.

According to literature scientific information and our own analytical data, there is in general a considerable variability of trace metal concentrations between different species, tissues and even between individuals captured from the same locations. This is due to the fact that, adtionally to the contamination degree of the marine environment, trace metals bioaccumulation is influenced also by the biological parameters, which include the permeability of the external surfaces, feeding habits, the presence of internal ligands, excretory systems efficiency, nutritional status, growing and reproductive stage, etc. (DEPLEDGE, 1990).

By combining absorbtion, elimination and storage processes, marine organisms, for example fish, are teoretically capable to regulate body trace metal concentrations, in spite of their level modifications in the environment. While on the contrary, bivalve molluscs are trace metal bioaccumulators, reflecting the contamination degree of the marine environment and thus being suitable as trace metal pollution indicators. For instance, mussels from Constantza North locations investigated in 2002 had cadmium, copper and manganese levels about three times higher than goby samples captured from the same location.

CONCLUSIONS

- Trace metals (copper, cadmium, lead and manganese) average concentrations in seawater, sediments and biota, observed in 2002, evince a moderate decreasing tendency, comparing with previous years. Anthropogenic impact is noticeable in the locations affected by waste water discharges (especially in Constantza South, Eforie South and Mangalia), and also in the northern sector influenced by the fluvial contaminant input;
- Average trace metal values in seawater along the Romanian coastal area were situated below maximum admisible levels, according with national regulations;
- *Mytilus galloprovincialis* samples were characterized by tissular trace metal concentrations correlated in general with the contamination of their environment and, in most cases, higher than the values observed for marine fish;

- In the case of marine fish, only in some isolated situations, depending of species and capture area, increased concentrations, slightly beyond maximum admisible limits, have been recorded.

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