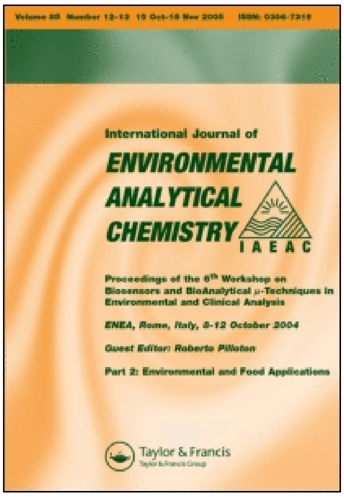

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A Comparison on Five Sediment Decomposition Procedures for Determining Anthropogenic Trace Metal Pollution

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A COMPARISON ON FIVE SEDIMENT DECOMPOSITION PROCEDURES FOR DETERMINING ANTHROPOGENIC TRACE METAL POLLUTION

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Five different procedures of sediment decomposition were compared, for evaluating the one more appropriated for assessing anthropogenic metal pollution. Exchangeable-metal extraction in sodium acetate, weak extraction in hydroxylamine hydrochloride/acetic acid, moderate extraction in diluted hydrochloric acid, oxidising strong acid digestion and total decomposition with hydrofluoric acid were tested. The mildest sodium acetate attack, which gives also better account for the bioavailable metal fraction, is the more effective in enhancing differences between polluted sediments and nonpolluted ones. Copper, lead and zinc are the best indicators of trace metal pollution of surface sediments.

Keywords: Sediment decomposition; polluted sediments; metal pollution

INTRODUCTION

For determining trace metal concentrations in marine sediments, it is necessary to dissolve the samples by a chemical attack: the more current procedures are the following: i) total decomposition by hydrofluoric acid, ii) strong acid digestion, and iii) weak acid extraction.[1] The choice of the attack procedure is settled by the information required to the analyst: *i.e.*, the geochemical characterisation of the sediments does require a hydrofluoric acid attack giving the total content of each metal, while the assessment of the degree of trace metal pollution to whom the sediment dwelling organisms are exposed can be better obtained by a milder attack. The total HF-attack allows to assess the accuracy by analysing certified

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reference materials. This attack is the most effective because it dissolves the silicate lattices: the so released metals, also defined as "residual" metals,[2] have natural sources (rock erosion, weathering, and so on); the other attacks do not dissolve the lattice-held metals, but only the "non-residual" metals which are less or more bounded/absorbed to the sediments: these metal fractions are likely due to more recent inputs in the sediments, mainly from anthropogenic sources. The noxious effects of the trace metals on the marine organisms are not necessarily proportional to their total content in the sediments (where they are accumulated as very low soluble compounds): the very smaller "bioavailable" fraction has more environmental relevance.

For assessing the pollution of sediments it is more appropriate an analytical procedure which enhances the difference in trace metal contents between the examined sediment, suspected of pollution, and a nonpolluted (or very low polluted) sediment, to be considered as a background sample.[3] In this report we discuss and compare the results of the five different single decomposition-extraction procedures: the chosen procedures ask for both precision and simplicity, for detecting the non-residual metals. The Sequential extraction procedures (SEP) proposed by BCR[4] are rather intended to define the different bioavailable fractions of metals in sediments. This approach, studied by several authors,[5–7] is beyond of our purpose.

In the present paper we chose the following procedures of increasing strength: "exchangeable-metal" extraction in sodium acetate;[8] weak extraction in hydroxylamine hydrochloride-acetic acid,[9–10] moderate extraction in dilute HCl;[2,11,12] oxidising strong acid digestion in HNO_3-H_2O_2-$HClO_4$;[13] and total decomposition in HF-HNO_3.[1] We applied these procedures to determine copper, lead, cadmium, zinc, chromium and nickel in marine sediments sampled in the inner harbour of Trieste (North-eastern Italy), an area with intense industrial and shipping activities, where profound depletion and alterations of the benthic fauna were observed.[14]

EXPERIMENTAL

Sample collection

Surface sediments were collected in October 1995; a Van Veen grab sampler was used, taking samples of about 0.2 m^2 and penetrating up to a depth of about 15 cm, at seven sites (labelled in Figure 1, from 1 to 7) along a transect of about 2.5 km going from the shore towards the dam-line closing the inner harbour of

Trieste. The samples were cooled (4°C) for transport in laboratory, where the coarse material (>2 mm) was removed. The freeze dried remaining material was homogenised and sieved: the fraction <200 μm [15] was used for analysis. All the steps preceding the chemical analysis were detailed in previous works.[14,16]

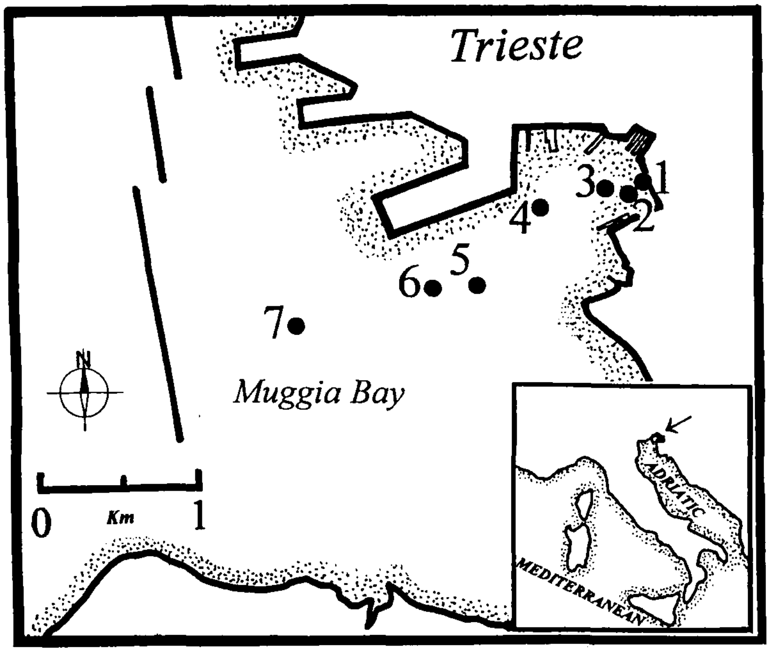

FIGURE 1 Seven sample sites in the harbour of Trieste

Sediment decomposition procedures

The weighted dry sediments were suspended in the respective attack solutions, thereafter listed in order of increasing strength from (*a*) to (*e*), and stirred at room temperature (attacks *a*, *b*, *c*) or heat digested by a programmed Milestone MLS1200 microwave System (attacks *d*, *e*). The sample amount depended on the expected metal concentrations: the weakest attack (*a*) needed about 2.0 g of dry sediment sample, but only 0.2 g of sample was sufficient for the strongest attack by HF (*e*). The so obtained suspensions were centrifuged, the decanted solutions were filtered and made up to 50 mL with ultrapure MilliQ water, and then transferred in polyethylene bottles for storage before analysis. The ratios between dry sediment weights and chemical reactants (all of analytical grade) were as follow for the five decomposition procedures:

a. "exchangeable-metal" extraction:[8] 2.0 g of dry sediment were stirred for 1 hour in 16 mL of sodium acetate 1 M (pH 8.2);
b. weak extraction:[9,10] 2.0 g of dry sediment were stirred for 6 hours in 40 mL of a 0.04 M solution of hydroxylamine hydrochloride in acetic acid (25% v/v);
c. moderate extraction:[2,11,12] 2.0 g of dry sediment were stirred for 16 hours in 20 mL of HCl 0.5 M;
d. oxidising strong acid digestion:[13] 0.5 g of dry sediment were suspended in 3.0 mL of HNO_3 (65%), 0.1 mL of H_2O_2 (30%) and 0.1 mL of $HClO_4$ (70%); this suspension was microwave heated in Teflon vessels;
e. total decomposition:[1] 0.2 g of dry sediment were suspended in 2 mL of HF (48%) and 2 mL of HNO_3 (65%), and microwave heated in teflon vessels; 0.5 g of boric acid crystals were then added to the cooled solutions.

Analytical measurements

All solutions obtained by the five decomposition procedures were analysed by flame atomic absorption spectroscopy (FAAS): a spectrometer Varian SPECTRAA20 was used. The metal concentrations of copper, lead, cadmium, zinc, chromium and nickel were evaluated by using calibration curves obtained with multielement standard solutions. A decomposition blank, constituted by the reagents used through each decomposition procedure, was used for preparing the working standards, in order to compensate the matrix effects.[1] Cadmium concentration was very low in some cases; consequently, we have analysed all the samples in parallel for cadmium by differential pulse anodic stripping voltammetry (DPASV).[17,18]

Each sample was measured in triplicate: a relative standard deviation (RSD%) between 5 and 10% was obtained in our working ranges. The accuracy was verified for the total decomposition procedure (*e*) by using a certified reference material (BCSS-1, Marine Sediment Reference Material for trace metals and other constituents, by National Research Council Canada).

RESULTS AND DISCUSSION

We have determined Cu, Pb, Cd, Zn, Cr and Ni in each of the 7 samples collected along the transect (see Figure 1); the metal content values obtained by the five decomposition procedures reported in the Experimental Section (from *a*, the weakest, to *e*, the strongest) are listed in Table I. For the sake of comparison, the values obtained from BCSS-1 are reported in the last line (certified values for procedure *e* are in brackets).

TABLE I Metal content values (μg g^{-1} dry wt.) obtained by the five attacks (*a-e*) on sediments of sites from 1 to 7, and on BCSS-1 certified sediment (certified values are given in brackets)

Sample	*Cu*					*Pb*					*Cd*				
	a	*b*	*c*	*d*	*e*	*a*	*b*	*c*	*d*	*e*	*a*	*b*	*c*	*d*	*e*
1	4.42	59.2	176	390	401	4.22	237	263	341	509	<0.02	<0.02	0.73	7.40	15.4
2	3.64	58.7	186	374	381	2.46	218	370	494	510	<0.02	<0.02	0.47	5.96	16.3
3	0.48	36.2	112	216	218	2.32	193	169	220	272	<0.02	<0.02	0.53	5.45	16.6
4	0.19	37.4	99	205	227	2.72	200	221	263	667	<0.02	<0.02	0.54	5.74	33.0
5	0.20	11.4	29.4	60.1	75.0	0.20	105	191	279	455	<0.02	<0.02	0.63	6.79	14.7
6	0.20	11.2	31.7	58.5	75.8	0.69	61.9	152	196	202	<0.02	<0.02	0.39	4.35	18.7
7	0.10	7.93	26.2	50.7	71.4	0.89	49.3	127	166	260	<0.02	<0.02	0.21	4.20	18.7
BCSS-1	0.10	3.4	9.8	16.7	19.7 (18.5)	1.00	5.7	17.0	25.3	26.1 (22.7)	<0.02	<0.02	<0.02	0.20	0.29 (0.25)

Sample	*Zn*					*Cr*					*Ni*				
	a	*b*	*c*	*d*	*e*	*a*	*b*	*c*	*d*	*e*	*a*	*b*	*c*	*d*	*e*
1	4.03	740	729	879	1122	<0.50	17.0	19.2	34.4	117	<0.50	29.8	29.4	74.0	320
2	3.25	749	689	835	1088	<0.50	16.2	21.9	29.2	124	<0.50	28.5	32.2	76.1	397
3	0.58	520	505	616	743	<0.50	16.8	17.8	32.0	129	<0.50	29.2	35.0	75.4	371
4	1.65	587	519	670	1096	<0.50	15.4	20.9	33.2	136	<0.50	28.6	32.2	76.5	414
5	0.29	202	182	367	445	<0.50	11.6	18.1	29.4	135	<0.50	25.8	29.4	79.3	405
6	0.20	144	160	290	379	<0.50	10.9	17.8	33.1	116	<0.50	23.6	29.3	77.6	343
7	0.10	141	154	277	524	<0.50	10.2	21.8	29.7	133	<0.50	24.5	33.7	78.0	400
BCSS-1	0.40	40.7	93.0	107	110 (119)	<0.50	1.1	36.8	52.1	116 (123)	<0.50	3.2	20.3	56.9	60.5 (55.3)

The extracted fraction of trace metals depends not only on the decomposition procedure, but on the specific metal element; the matrix effect has minor influence: we have verified that all samples have similar grain size and mineralogical composition.

The histograms of Figure 2 show the recovery percentages for the 6 metals, as obtained by the four milder attacks (*a-d*), referred to the HF-attack (*e*). We can distinguish between copper, lead, zinc and cadmium on one side, and chromium and nickel on the other side. In fact, Cu, Pb and Zn give high recoveries also by the milder attacks, whereas Cr and Ni give recoveries below 20% also by strong oxidising acid attack. Owing its very low concentrations, Cd gives good recoveries only with attack *d*: attacks *a* and *b* give data below the limit of detection.

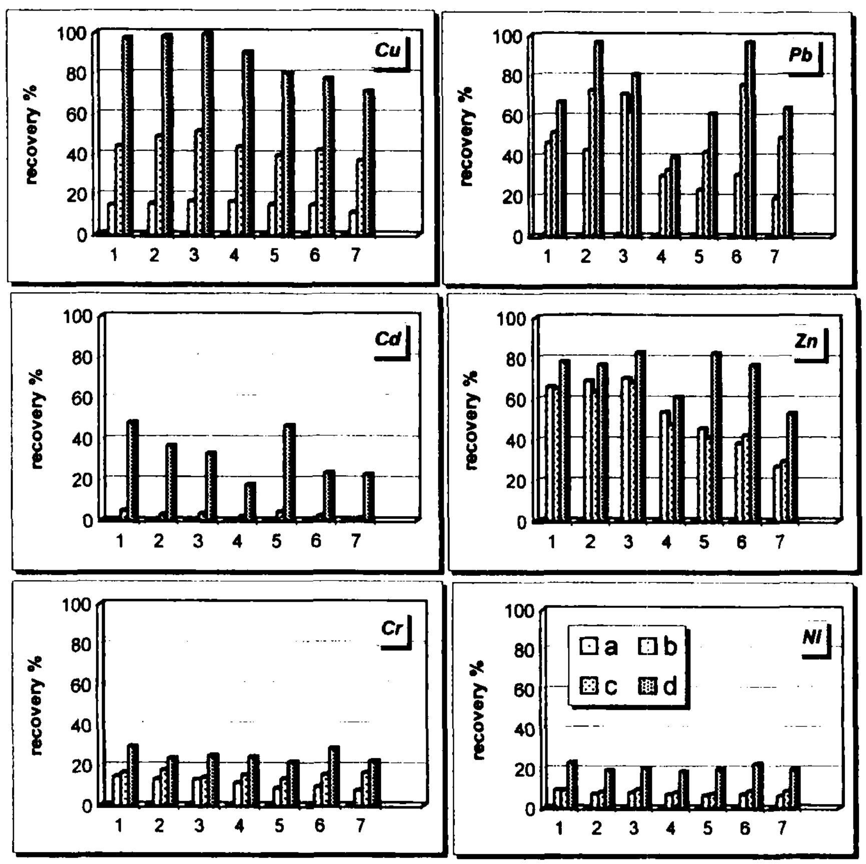

FIGURE 2 Recovery percentages for the 6 trace metals as obtained by *a*, *b*, *c*, *d* attacks, referred to the total HF-attack

It is now interesting to find out which of the five procedures is most effective in enhancing the difference in trace metal contents between a polluted sediment and a nonpolluted one considered as a background. The trace metal concentration data reported in Table I show - only for Cu, Pb and Zn – a decreasing gradient going from the shoreline towards the more external sites, near the dam-line; so we can consider the shoreline (Site 1) as a point-source of metal pollution, and the remote Site 7, with the lowest metal contents, as a background. We have computed the ratios (R):

$$R = \frac{\left(\begin{array}{c} \textit{metal content} \\ \textit{in polluted sediment} \end{array} - \begin{array}{c} \textit{metal content} \\ \textit{in background sediment} \end{array}\right)}{\textit{metal content in background sediment}}$$

for the Sites 1–6 (taking Site 7 as background), using the metal contents obtained by the five attack procedures (*a-e*).

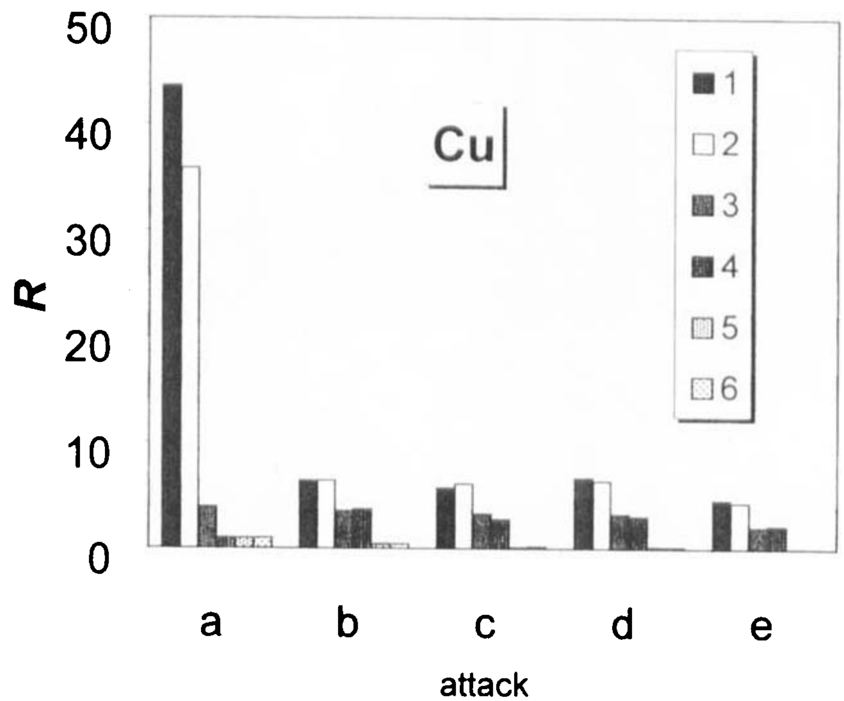

FIGURE 3 Copper *R*-values obtained by five attacks (*a-e*) on sediments of different sites (from 1 to 6)

Copper, lead and zinc are the metals with the highest ratios, reflecting the difference in trace metal contents between the polluted sediment and the background; on the other side, we found again chromium and nickel with very low ratios: *i.e.*, these latter metals are not able to differentiate polluted sediments from nonpolluted ones.

We have plotted R-values as histograms (see Figures 3, 4 and 5), focusing our attention on the three "indicator" metals, namely Cu, Pb and Zn, that better allow to detect the anthropogenic metal pollution in sediments.

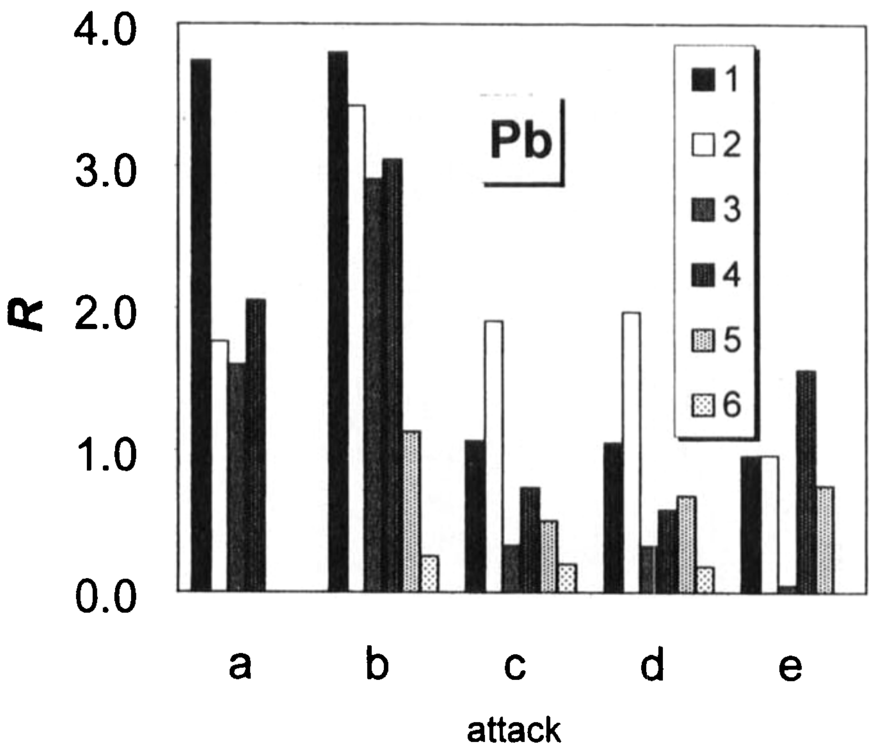

FIGURE 4 Lead R-values obtained by five attacks (a-e) on sediments of different sites (from 1 to 6)

It can be interesting to evaluate the effectiveness of the 5 decomposition procedures in determining the anthropogenic metal fraction: the histograms show clearly that the mildest procedure (a) results as the more effective for evaluating the pollution degree of a sediment, although it gives very dilute solutions. For lead, both procedures a and b have the same capability. It is worth noting that simply stirring the sediment for 1 hour in 1 M sodium acetate we are able to detect concentrations of Cu and Zn in Site 1 (the most polluted) that are 40 times higher than in the external Site 7, taken as background. Furthermore, this extrac-

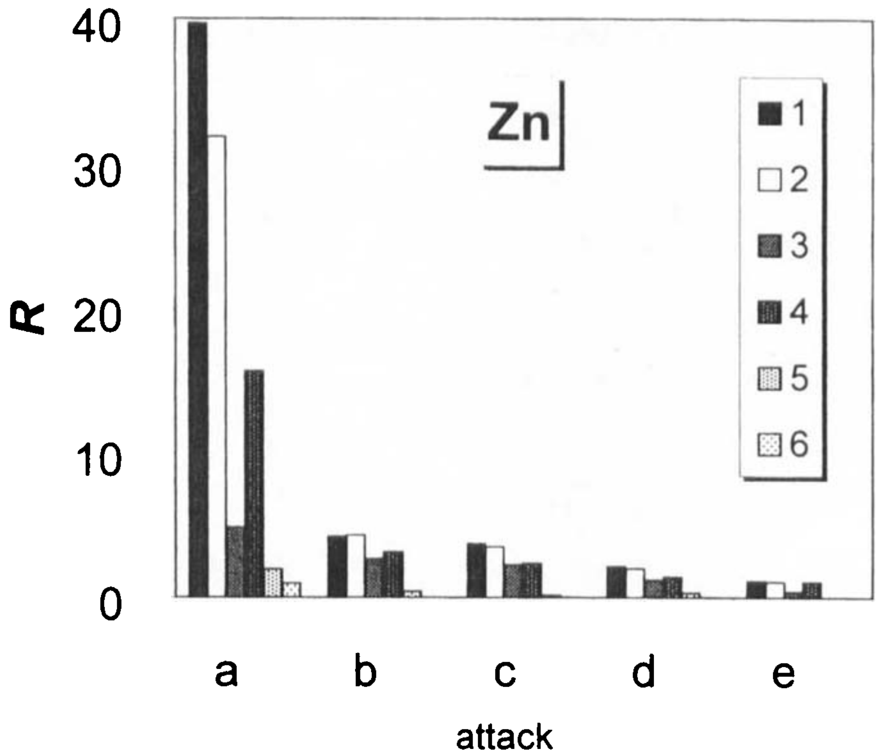

FIGURE 5 Zinc *R*-values obtained by five attacks (*a-e*) on sediments of different sites (from 1 to 6)

tion procedure, using a solution at pH 8.2, is the one that better mimics the conditions that produce the bioavailable metal fraction, affecting the life of the benthic environment.

CONCLUSIONS

The main purpose of this study was to verify which sediment decomposition procedure is more suited for assessing the degree of trace metal pollution, in a precise and simple way. The intercomparison of the analytical data obtained by five decomposition procedures of increasing strength allows us to conclude that the mildest attacks are the most effective in enhancing the difference between polluted sediments and nonpolluted ones in terms of their trace metal contents. At the same time, the so obtained metal content values give a better account for the bioavailable fraction, and, as a consequence, on the toxicity of the sediments for the benthic organisms. Between the here considered trace metals, copper, lead and zinc are the best "indicators" of trace metal pollution for these surface sediments.

We intend the mild "exchangeable-metal" extraction as appropriate for environmental monitoring of areas suspected of pollution, that requires to analyse many samples, with constraints of cost and time; and we have planned to extend the samplings to a grid of sites in the harbour of Trieste, on the purpose to verify possible different sources of metal pollution.

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