WHAT IS THE DIGESTATE?

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SUMMARY
As anaerobic digestion (AD) is quickly being harnessed in Italy and in other European countries, there is a need for a more in-depth description of the main by-product of the process, the digestate. Little information on digestate characteristics and composition is available and unclear legislation causes problems in biogas plant management. In this work, the organic matter (OM) of this matrix was described through chemical, biological, spectroscopic, and statistical approaches. It was shown that AD results in a strong reduction of the easily degradable fraction of the OM and an accumulation of recalcitrant molecules (possible humus precursors). This contributes to a relatively high biological stability of the residual OM content in the digestate and may lead to good amendment properties. Besides, the observed relative accumulation and the high mineralisation of nitrogen and phosphorus may point to the digestate as a readily available liquid fertiliser for agronomic use. Moreover, xenobiotics and pathogens respected limits for both biosolids and compost in Italian and European legislation.

1. INTRODUCTION
Anaerobic digestion (AD) is a biological process that transforms the initial substrate (ingestate) into the desired product (biogas) and into a solid-liquid by-product (digestate) (Cecchi et al., 1988).
Products such as compost and biosolids from sewage treatment plants are already well-known and, in Europe, legislation clearly regulates their

agronomic use or disposal. Therefore, while clear information on these products is readily available, data on digestates from AD processes are scarce. In Italy, for example, legislation involving use of digestate is completely deficient compared with those dealing with compost and biosolids. This is due to the lack of information about digestate composition, its agronomic properties and the potential environmental impacts or benefits connected to agronomic reuse or disposal.

The literature reports only a little information about digestate; we know that many organic molecules, such as carbohydrates, proteins, lipids, cellulose and others, are totally or partially biodegraded to some gaseous products (methane, carbon dioxide) and also transformed into molecules forming microbial cells (Muller et al., 1998, Connaughton et al, 2006). Nevertheless, nothing is known about the chemical and biological characteristics of the digestate and of the changes that occur during AD.

The aims of this study were to analyse these modifications in depth and to describe the composition and characteristics of the digestates using chemical, biological, spectroscopic and statistical analyses.

2. MATERIALS AND METHODS

Twelve ingestates and the consequent digestates were sampled from a full-scale biogas plant co-digesting swine manure, various energy crops, organic residues and the organic fraction of municipal solid waste (OFMSW).

Chemical analyses were performed to determine organic matter (OM) content and degradation yields in terms of mass balance of total solids (TS), volatile solids (VS), biochemical oxygen demand (BOD_5,) and chemical oxygen demand (COD) between ingestates and digestates. The OM quality was then determined through wet analyses, i.e., cell solubles (CS), acid detergent lignin (ADL), cellulose, and hemicellulose. Biological stability and degradability were determined by two biological tests: oxygen demand in 20 h (OD_{20}) and anaerobic bio-gasification potential test (ABP). The most important nutrient concentrations (total, mineral and organic nitrogen, total phosphorus) were also measured in both ingestates and digestates to determine their fate during the AD process. Representative samples were used to carry out all analytical tests. The TS and VS were determined according to standard procedures (APHA,

1998). Total Kjeldahl nitrogen (TKN) and ammonia were determined on fresh material, following the analytical method used for wastewater sludge (IRSA CNR, 1994; ISO, 1994). Analyses were performed to determine neutral detergent fiber (NDF), acid detergent fiber (ADF) and ADL, according to Van Soest method (Van Soest et al., 1991). Values of CS, ADL, cellulose (ADF-ADL), and hemicellulose (NDF-ADF) were calculated according to Van Soest et al. (1991). All analyses were done in duplicate. ABP and OD20 were determined following the methods of Schievano et al. (2008). Spectroscopic characteristics of the samples were studied by solid-state CP MAS ^{13}C-NMR analysis (this is a powerful technique for examining the chemical composition of complex OM, since it can be used on bulk samples). In particular, the CP MAS ^{13}C-NMR spectra on sample ingestates and digestates were acquired at 10 kHz on a Bruker AMX 600 spectrometer (Bruker BioSpin GmbH, Rheinstetten) using a 4-mm CP-MAS probe. The pulse repetition rate was set at 0.5 s; contact time was 1 ms and the number of scans was 3200. The chemical shift scale of CP MAS ^{13}C-NMR spectra was referred to tetramethylsilane (d = 0 ppm).
To compare results, the same analyses were carried out on samples of compost (90-d aerobic stabilisation), bio-solid, and fresh and pre-digested pig slurry. All results describing OM quality were analysed using principal component analysis (PCA) (Tabachnick and Fidell, 2001). PCA is a multivariate statistical technique used to investigate the relationships among quantitative variables. Its use allows a number of variables to be reduced in a multivariate data set, while retaining as much variation in the data set as possible. This reduction was achieved by taking p variables X_1, X_2, …, Xp and finding their combinations to produce principal components (PCs) PC_1, PC_2,…, PCp, which are uncorrelated.

3. ORGANIC MATTER DEGRADATION AND MODIFICATION DURING THE AD PROCESS

3.1. Chemical and biological approach

Considering both quantitative and qualitative aspects, the obtained results confirmed that AD greatly modifies the OM of an ingestate. Strong reductions (65±10%) in OM content, in terms of VS balance, were noticed (Figure 1a). In parallel, the COD and BOD_5 concentrations

in the digestate were almost half of the initial concentrations (Figure 1b and 1c).
The OM quality and degradability were also affected, as respirometric activity (OD_{20}) was halved in the digestates (Figure 1d) and the residual potential biogas (ABP) was almost one-third of the initial one (Figure 1e). Besides, a direct correlation between these two parameters, both representing biological stability of OM (D'Imporzano and Adani, 2007, Schievano et al., 2008), was found (Figure 2). This finding confirmed the observation that biological stability increases during AD, suggesting that degradation processes determine a concentration of the more recalcitrant molecules, while the more easily degradable matter is transformed into biogas. Further confirmation was obtained from the results of the wet analyses (Figure 3). The more degradable fractions, represented by the CS, significantly decreased in the digestates, while recalcitrant molecules, measured with the ADL, strongly accumulated. Other kinds of molecules such as cellulose and hemicellulose resulted in almost constant percentages of TS. This means that, as TS content decreased during AD, cellulose and hemicellulose degradation occurred, even at a lower extent, when compared with CS.

3.2. Spectroscopic approach

The results obtained from the chemical and biological approach were confirmed in the spectroscopic analysis. The spectra obtained by NMR showed four regions representing four different types of organic molecules (Figure 4), respectively from left to right, the carboxyl-C, the aromatic-C, the O-alkyl-C, and the aliphatic-C. Comparing the spectra of one of the considered ingestates and its relative digestate, the more degradable molecules,(the region of the O-alkyl-C [polysaccharides]), resulted in a net decrease in the digestate, while the more recalcitrant OM fraction (first, second, and fourth regions), evidently resulted in a relative increase. This confirmed the relative accumulation of molecules containing carboxyl-C, aromatic-C, and aliphatic-C, which include more recalcitrant fractions such as lignin, cutin, humic acids, steroids, and complex proteins. Similar results were found by comparing the spectra of fresh and digested pig slurries, even though the effect was less visible. This was due to a lower concentration of easily degradable molecules in the OM, with respect to the ingestate.

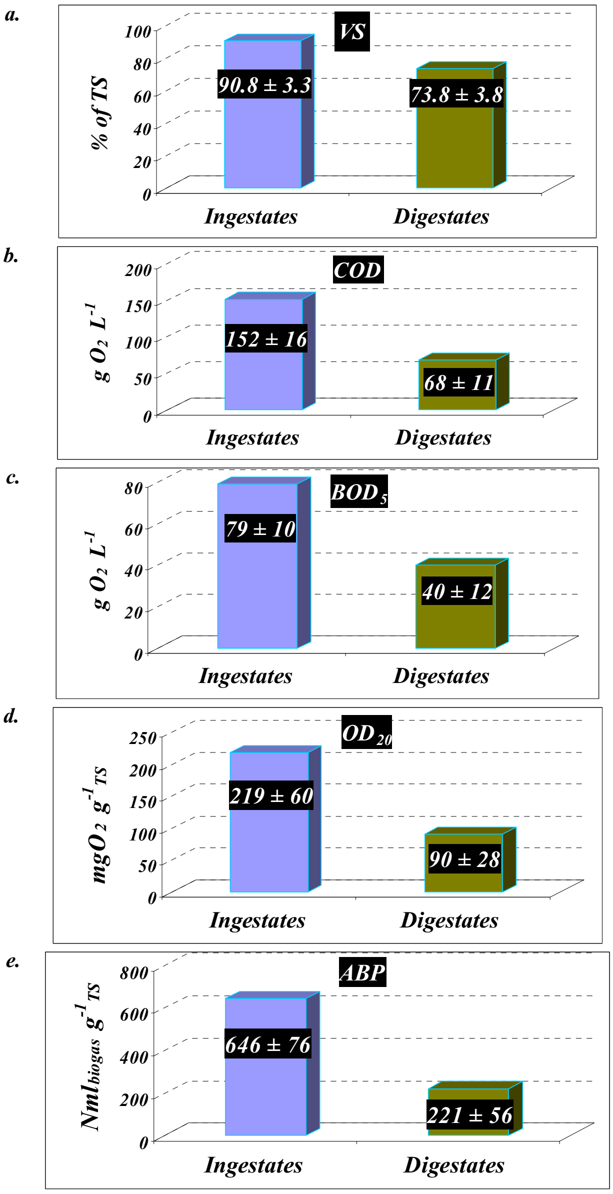

Figure 1. *Organic matter degradation during AD process: chemical and biological approach, a. Volatile solids, b. Chemical oxygen demand, c. Biochemical oxygen demand, d. Oxygen demand in 20 h, e. Anaerobic biogasification potential.*

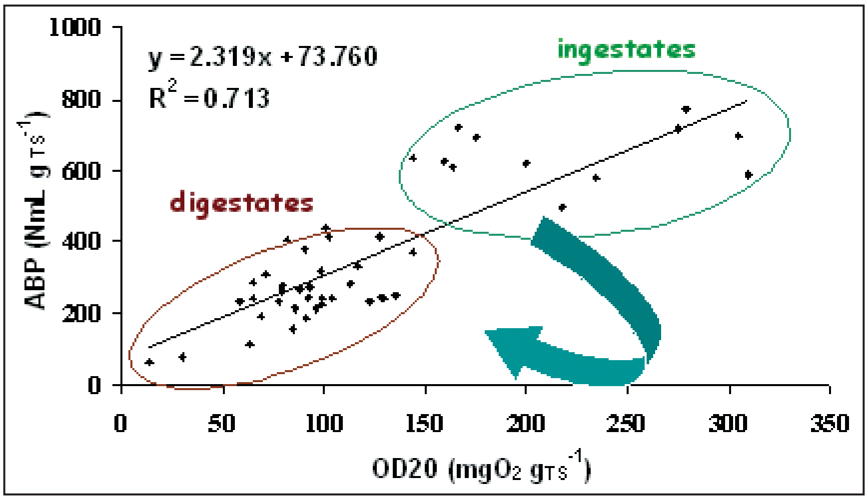

Figure 2. *Changes in OM quality and degradability during the AD process: correlation between ABP and OD_{20}.*

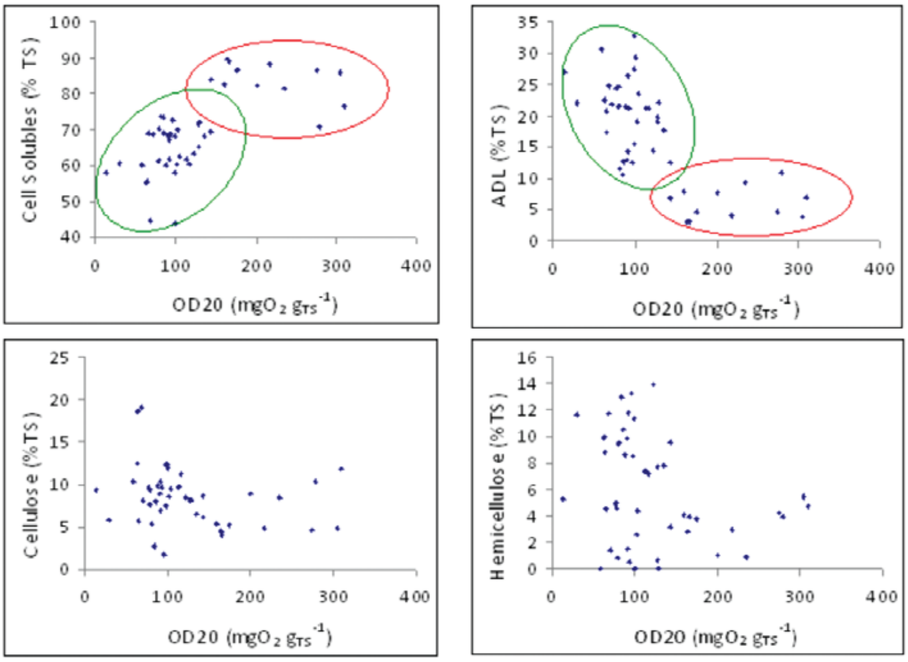

Figure 3. *Changes in OM quality during AD process: wet analyses. Ingestates (red circle); digestates (green circle).*

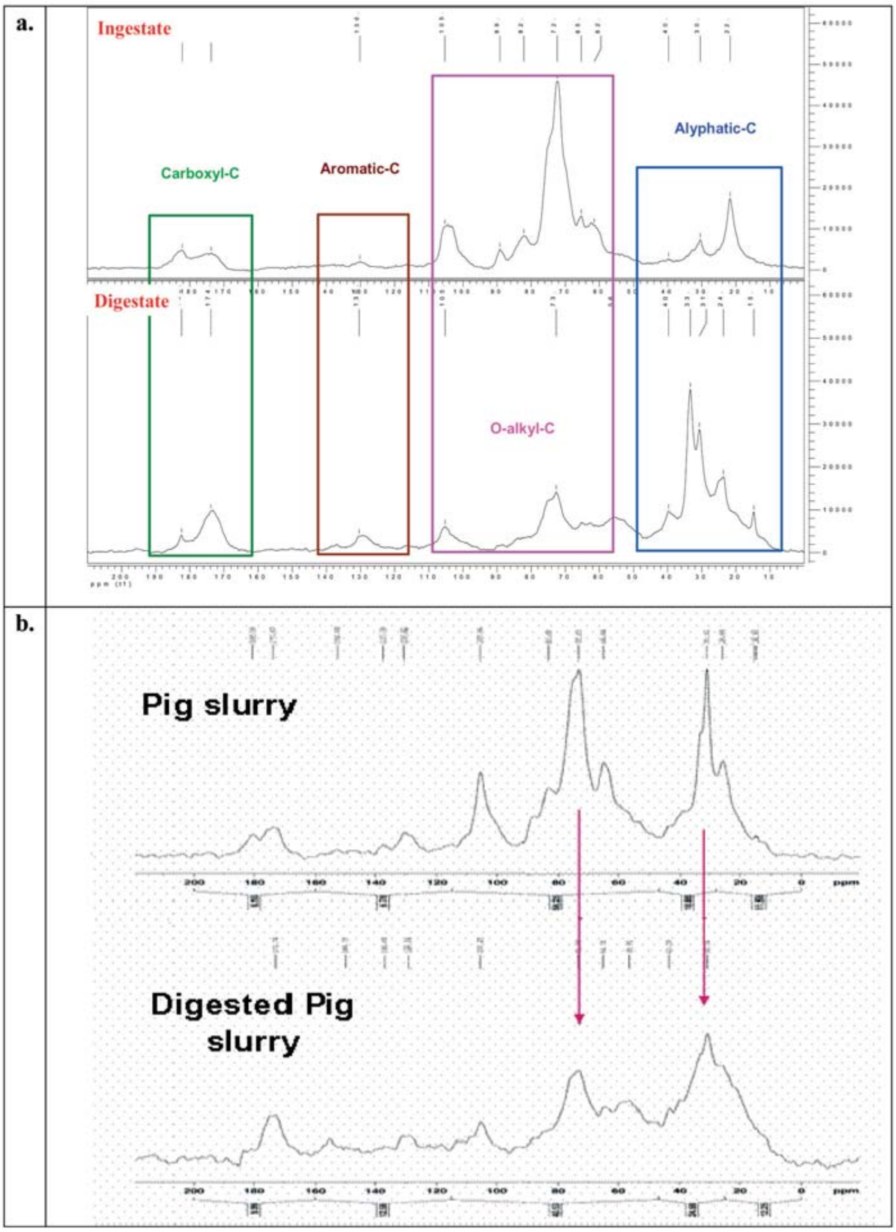

Figure 4. *CMAS ^{13}C-NMR spectra. a. Comparison between ingestate and digestate. b. Comparison between pig shurry before and after AD.*

3.3. Statistical approach: PCA

The PCA method resulted in a more accurate and complete description of the quality of the OM in the digestate, in comparison with other organic matrices. The quantitative variables considered were biological parameters (ABP, OD_{20}), chemical composition (VS content), and the NMR responses on carbon links, i.e., aliphatic-C, aromatic-C, carboxyl-C, and O-alkyl-C. The biplot obtained from PCA results (Figure 5) showed that the first component, which explained 63.8% of the total variance, was positively and highly correlated (r>0.6) with ABP, OD_{20}, VS, and O-alkyl C and negatively correlated with aliphatic-C, aromatic-C, and carboxyl-C. The second component, which explained 31.9% of total variance, was positively and highly correlated (r>0.6) with aliphatic-C and negatively correlated with O-alkyl-C and aromatic-C fractions.

Therefore, the first component represents a biological stability gradient (the biological stability value increases from negative to positive PC_1 value). Besides, PC_2 can be associated with the type of carbon links. The ingestate was in the fourth quadrant, i.e. low biological stability and high presence of O-alkyl-C (easily biodegradable fraction). The fresh swine manure was located in the first quadrant because of limited presence of O-alkyl-C. The pre-digested swine manure, the digestate, and the bio-solid were all located in the second quadrant, indicating medium-high biological stability and prevalence of aliphatic-C fraction. The compost was in the third quadrant due to a medium-high level of biological stability and a high concentration of recalcitrant fraction (aromatic-C fraction). That probably depends on the lignocellulosic material normally contained in compost.

Therefore, the digestates had high biological stability, showing values very similar to compost. Italian law allows the agronomic use of stabilised compost and bio-solids. It can be concluded that the digestate can be considered a good organic amendment, thanks to the concentrate recalcitrant and humus-precursor molecules, which enhance soil quality and agronomic properties.

3.4. Nutrients

The literature says that macronutrient total content tends to be not influenced or is only slightly decreased during AD processes (Massè et al., 2007, Uludag-Demirera et al., 2008). This was confirmed by the

accumulation observed in this study of both total N and total phosphorus (Fig. 6). In fact, while degradable OM was transformed into biogas, the relative content of nutrients in the TS increased proportionally to biological stability (Fig. 6).
A high accumulation of ammonia was observed, whereas organic N percentage on the TS was constant. This indicates a net mineralisation of N during AD. Sørensen and Møller (2008) demonstrated that AD of animal slurries, as it increases the mineral N to organic N ratio, enhances the efficiency of N assimilation by the crop because ammonia is a soluble form of N, which is readily available to the plants in a soil-crop system. Besides, N losses in the form of leached nitrates and volatilised ammonia are reduced. Therefore, AD increases the efficiency of N utilisation, by transforming organic N into mineral N. The obtained efficiency is comparable with that of mineral fertilisers (Sørensen and Møller, 2008).

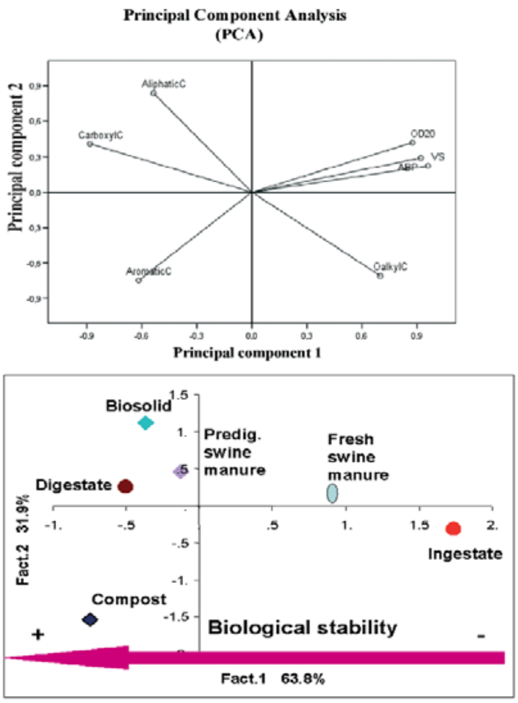

Figure 5. *Principal component analysis: a comparison of OM quality and composition of an ingestate, a digestate and other organic matrices.*

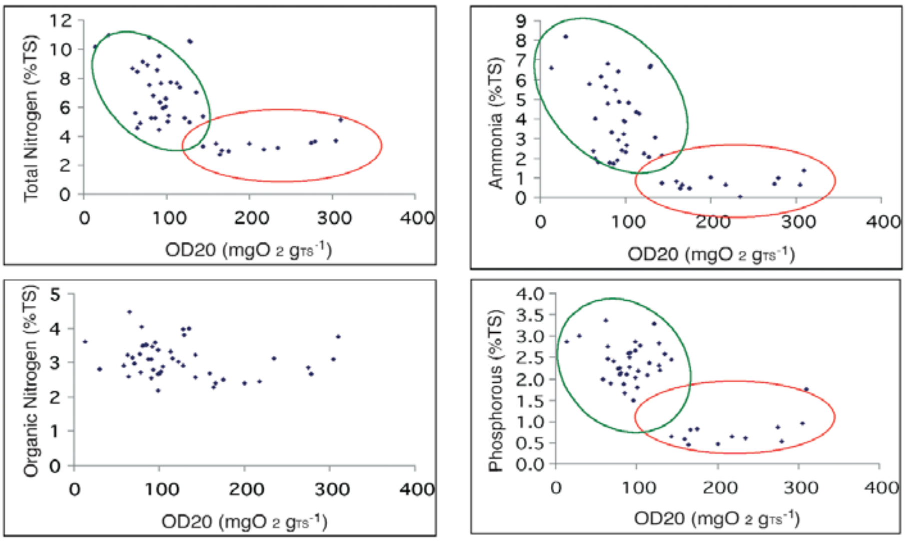

Figure 6. *Changes in N and phosphorous content during the AD process. Ingestates (red circle); digestates (green circle).*

4. XENOBIOTICS AND HYGIENIC PARAMETERS

The most important xenobiotics, the same variable considered in defining the quality of composts and bio-solids, were measured and found to be within standard limits of concentration for both compost and bio-solid (Table 1). The same result was obtained for the main hygienic parameters (Table 1).

It must be noted that the analysed digestates were sampled from a full-scale biogas plant processing OFMSW, which is a matrix that may present risks of containing pollutants or pathogens.

Table 1. *Xenobiotic concentrations and hygienic parameters in the digestate (ni = not indicated).*

Metal	**Value**	**Biosolid Limit**	**Compost Limit**
Cd (mg kg_{TS}^{-1})	0.21	20	1.5
Hg (mg kg_{TS}^{-1})	1.19	10	1.5
Ni (mg kg_{TS}^{-1})	12.48	300	100
Pb (mg kg_{TS}^{-1})	18.16	750	140
Cu (mg kg_{TS}^{-1})	49.58	1000	230
Zn (mg kg_{TS}^{-1})	74.83	2500	500
Cr (mg kg_{TS}^{-1})	1.16	750	-
As (mg kg_{TS}^{-1})	0.05	10	-
Cr VI (mg kg_{TS}^{-1})	0.08	10	0.5
Hygienic Parameter	**Value**	**Biosolid Limit**	**Compost Limit**
Fecal Coliform (MPN g^{-1}_{TS})	100	10	n.i.
Vital Helminthes eggs	Absent	Absent	n.i.
Salmonella	Absent	<100	Absent
Escherica coli	Absent	n.i.	<1000

5. CONCLUSIONS

An identification of the digestate was provided, focusing on various aspects such as OM amount, composition, quality and stability, nutrient content, and concentrations of xenobiotics and pathogens.

The results showed large reductions in OM amount during the AD process and a relatively high biological stability of the residual OM. Compared with other kinds of digested matrices, only compost showed a higher stability. Moreover, a concentration of recalcitrant fractions such as aromatic and aliphatic molecules, which are possible humus precursors, was evidenced. Thus, the digestate may be considered to have good amendment properties. The content of the considered nutrients (total N and P) tended not to be influenced during the AD process. At the same time, N was shown to be mineralised at a high extent and to concentrate as ammonia. As ammonia is a readily available source of N for plants, the digestate may be act as a good fertiliser.

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