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# THE POTENTIAL OF γ-RAY SPECTROSCOPY FOR SOIL PROXIMAL SURVEY IN CLAYEY SOILS

# LE POTENTIEL DE LA SPECTROSCOPIE A RAYONS-γ LORS DE L'ECHANTILLONNAGE PEDOLOGIQUE DE SOLS ARGILEUX

# LE POTENZIALITÀ DELLA SPETTROSCOPIA DI RAGGI-γ NEL RILEVAMENTO PEDOLOGICO DI SUOLI ARGILLOSI

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## Abstract

Gamma-ray spectroscopy surveys the intensity and distribution of γ-rays emitted from radionuclides of soils and bedrocks. The most important radionuclides of soils and rocks are: $^{40}$K, $^{232}$Th, $^{238}$U and $^{137}$Cs, the latter due to Chernobyl explosion or radioactive pollution. Distribution and quantity of these radionuclides in the soil are strictly linked to parent material mineralogy and soil cation exchange capacity.
The aim of this work was to show the potential results of γ-ray proximal survey spectroscopy within experimental fields of clayey soils in western Sicily. The γ-ray spectrometer used for the fieldwork was "The Mole", made by "The Soil Company", "Medusa system" and the University of Groningen, Netherlands. During the survey of eight experimental fields, 55 soil samples were collected for laboratory analysis of particle size distribution, calcium carbonate, organic carbon and total nitrogen content. The results of the work show the statistical correlations between soil features and γ-ray data.
**Keywords**: *soil proximal sensing, radiometry, soil mapping, carbon stock, precision agriculture*

## Résumé

La spectroscopie aux rayons γ mesure la répartition et l'intensité du rayonnement gamma émis naturellement par les sols ou les roches. Les radionucléides les plus importants dans le sol comme source de rayons gamma sont : $^{40}$K, $^{232}$Th, $^{238}$U et $^{137}$Cs, ce dernier d'origine artificielle, principalement en raison de l'explosion de Chernobyl ou de la pollution radioactive. La distribution et la quantité de ces radionucléides est strictement dépendante de la minéralogie du matériau de base et de la capacité d'échange cationique du sol. Le but de ce travail était de montrer le potentiel de détection proximale par spectroscopie aux rayons γ dans des champs

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expérimentaux ~~avec~~ de sols argileux de la Sicile occidentale. Le spectromètre aux rayons γ utilisé dans ces champs était "The Mole", mis au point par les sociétés "The Soil Company", "Système Medusa" et l'Université de Groningen (Pays-Bas). Pendant l'étude des huit champs d'expérimentation ont été collectés 55 échantillons de sol pour analyse au laboratoire de la taille des particules, de la teneur en carbonate de calcium, du carbone organique et de l'azote total. Les résultats de ces travaux montrent les corrélations statistiques entre les caractéristiques du sol analysés et les données de spectroscopie aux rayons γ.

**Mots-clés:** *échantillonnage proximal, radiométrie, cartes des sols, stock de carbone, agriculture de précision.*

## Riassunto

La spettroscopia di raggi-γ misura la distribuzione e l'intensità della radiazione gamma emessa naturalmente dai suoli o dalle rocce. I radionuclidi più importanti nel suolo come fonte di raggi gamma sono: $^{40}$K, $^{232}$Th, $^{238}$U ed $^{137}$Cs, quest'ultimo di origine artificiale, principalmente legato all'esplosione di Chernobyl o ad inquinamenti radioattivi. La distribuzione e la quantità di questi radionuclidi è strettamente dipendente dalla mineralogia del *parent material* e dalla capacità di scambio cationico del suolo. Scopo di questo lavoro è quello di mostrare le potenzialità di un rilevamento prossimale con spettroscopia di raggi-γ in campi sperimentali con suoli argillosi della Sicilia occidentale. Lo spettrometro di raggi-γ utilizzato in campo è stato il "The Mole", sviluppato dalle aziende "The Soil Company", "Medusa system" e dall'Università di Groningen (Olanda). Durante il rilevamento di otto campi sperimentali sono stati prelevati 55 campioni di suolo per le analisi di laboratorio per granulometria, contenuto di carbonato di calcio, carbonio organico e azoto totale. I risultati di questo lavoro mostrano le correlazioni statistiche tra i caratteri del suolo analizzati e i dati della spettroscopia di raggi-γ.

**Parole chiave**: *rilevamento prossimale, radiometria, cartografia pedologica, stock di carbonio, agricoltura di precisione.*

## Introduction

The use of γ-ray spectrometry for mapping radioelement concentrations in soils and rocks has been used since the sixties for mineral exploration and geological mapping, by airborne, ground and laboratory spectrometry. In the last decade, developments of γ-ray spectroscopy, like new detectors, multichannel analyzers and improvements of data processing and analysis, also provided efficient techniques for soil proximal sensing.

In fact, soil γ-radiation is mainly influenced by the bedrock and parent material mineralogy, but also by soil weathering and soil features.

The γ-ray photons have discrete energies, which are characteristic of the radioactive isotopes from which are caused (IAEA, 2003). Many natural elements have radioactive isotopes, but only potassium, uranium and thorium decay series produce sufficient energy and intensity to be measured by γ-ray spectrometry. These decay series have the greatest intensity for the energy ranges of 1.37-1.57 MeV for potassium ($^{40}$K), 1.66-1.86 MeV for uranium ($^{238}$U) and 2.41-2.81 MeV for thorium ($^{232}$Th).

Other two radionuclides that can influence γ-ray spectra are caesium ($^{137}$Cs) and atmospheric radon ($^{222}$Rn). According to previous studies (Grasty, 1975; Cook et al., 1996) ninety percent of the measured γ-radiation is emitted from the upper 30-50 cm of the soil.

In soil, water content and bulk density are the most important factors that attenuate the signal. Gamma-rays move faster in air than in water and solid (Cook et al., 1996), and therefore a higher bulk density and water-content give a lower gamma-signal. Each 10% of water content, attenuates the signal of about 10% (IAEA, 2003). Even precipitation can have a strong influence on γ-ray spectroscopy, especially on uranium estimation. Dust particles in the atmosphere have $^{222}$Rn daughter products ($^{218}$Po, $^{214}$Pb and $^{214}$Bi among others), that during a precipitation arrive at the ground. Therefore, γ-ray surveying should not be carried out during rainfall or shortly thereafter (IAEA, 2003).

Taking into account all of these environmental factors, the γ-ray spectrometry can be successfully used for soil surveying (Wong and Harper, 1999; Viscarra Rossell et al., 2007, Dierke and Werban, 2013).

Several studies of airborne γ-ray spectrometry have identified relationships between γ-rays, soil type (Cook et al., 1996; Pracilio et al., 2006; Rawlins et al., 2007) and soil moisture (Carroll, 1981).

In the last decade, ground-based γ-radiometrics has been used for soil proximal survey to predict maps of soil texture (Viscarra Rossell et al., 2007; Van der Klooster, 2011; Dierke et al., 2011), gravel content (Pracilio et al., 2006), soil available potassium (Wong and Harper, 1999), pH and organic carbon (Dierke and Werban, 2013) or, more in general, to discriminate soil typologies (Herrmann et al., 2010). These ground-based studies reported better relationships between γ-radiometrics and soil features than those provided by airborne surveys.

Most of the authors concluded that the use of γ-radiometrics for soil mapping is strongly site-specific (Rawlins et al., 2007; Dierke and Werban, 2013), because of greater weight of the parent material mineralogy respect to the soil features. Therefore, soil properties prediction/mapping by γ-radiometrics needs to be calibrated in each surveyed area.

The aim of this work was to test the relationships between several soil parameters of the topsoil (0-30 cm), namely texture, calcium carbonate, organic carbon, and nitrogen, with γ-radiometric sensing in similar clayey soils and analogous lithology (marine clays and clayey flisches), but in different areas of western Sicily.

## Materials and methods

This work reported the results of γ-ray proximal sensing in four areas of western Sicily (Italy). Two adjacent arable fields were surveyed for each area: $DAT_a$ and

$DAT_b$, (12.643° E – 37.932° N) were southward Dattilo village (Trapani); $UMM_a$ and $UMM_b$, (12.728° E – 37.896° N) were southward Ummari village (Trapani), $SAL_a$ and $SAL_b$ (12.954° E – 37.772° N) and $SAM_a$ and $SAM_b$, (13.082° E – 37.689° N) were between Santa Margherita Belice and Sambuca di Sicilia town (Agrigento). According to the regional lithological map, the lithology of *DAT* and *UMM* was clayey and calcareous-clayey flysches of Paleogene period, whereas the lithology of *SAL* and *SAM* was clays, silty-clays and marls deposits of Pliocene period.

According to the 1:250,000 soil map of Sicily (Fantappiè et al., 2010), the selected areas had similar soils. *DAT* and *UMM* fields were mainly characterized by Vertic Calcisols, Calcaric Regosols and Fluvic Cambisols; the soils of *SAL* were Calcaric Cambisols and Calcaric Regosols, whereas the soils of *SAM* were Haplic Calcisols and Calcaric Vertisols. The studied areas were placed in "Soil region 62.2", described as hills of Sicily on clayey flysch, limestone, sandstone and gypsum, and coastal plains with Mediterranean subtropical climate (Costantini and Dazzi, 2013).

The γ-radiometrics survey was performed by "The Mole" sensor, made by "Medusa Systems", "The Soil Company" and the University of Groningen, The Netherlands (Van Egmond et al., 2010; van der Klooster, 2011). The Mole is a commercial γ-ray spectrometer with a CsI-crystal of 70x150 mm (Van Egmond et al., 2010). The Mole was carried within the fields in a dedicated backpack (Fig. 1) and it was connect to a GPS and a rugged laptop, which recorded coordinates and γ-ray spectra (about one spectra/second). Gamma-ray spectra were analysed by a Full Spectrum Analysis, using Gamman software (Medusa Systems). This method fitted the measured spectra with the spectrum of $^{40}$K, $^{137}$Cs, $^{238}$U, $^{232}$Th with an activity of 1 Bq/kg (Becquerel per kilogram), using a chi-square algorithm (Hendriks, 2001; Van der Klooster et al., 2011).

**Figure 1**
*"The Mole" γ-ray spectrometer in the field.*

The effect of soil moisture on the measured signal for this sensor was analyzed by Hendriks (2001). With increasing soil moisture, the intensity of the standard spectra decreased, but the shape of the spectra did not. For this reason, the γ-ray data, measured in different soil moisture conditions, were standardized to the dry soil (µd) conditions. The standardization was calculated by the equation of Beamish (2013):

$$\mu_d = \frac{\mu_w}{1+1.11w} \qquad [1]$$

where "µw" was the γ-rays measured in the field conditions and "w" was the soil moisture content (g $g^{-1}$). The maps of soil moisture content were obtained by the interpolation of moisture measured in 110 points (measured by thermo-gravimetric method), using cokriging and the Topographic Wetness Index (TWI) as covariate. The TWI maps of the fields were calculated by SAGA-Gis software using the DEM (Beven and Kirkby, 1979). Interpolation of γ-ray data in each field was performed by ordinary kriging. During the survey, an amount of 55 soil samples (0-30 cm) were collected for laboratory analysis. The samples were analysed for texture, calcium carbonate, organic carbon and total nitrogen using the official Italian methods (Mi.P.A.F., 1997; Mi.P.A.F., 2000).

Pedological data of the sampling points were correlated with γ-ray data to test the relationships among them.

## Results and discussion

The γ-ray total counts (TC) of the studied fields varied between 161 and 535 counts $sec^{-1}$ (Tab.1), and the highest contribution was given by $^{40}K$ radionuclide (mean = 32.5 Bq $kg^{-1}$). $^{232}Th$ and $^{238}U$ provided a mean of 4.7 and 4.4 Bq $kg^{-1}$, respectively (Tab.1). $^{137}Cs$ radionuclide provided values around zero, with very few points higher than 3 Bq $kg^{-1}$.

| | Total counts counts $sec^{-1}$ | $^{40}K$ Bq $Kg^{-1}$ | $^{232}Th$ | $^{238}U$ |
|---|---|---|---|---|
| Min | 161.3 | 0.0 | 0.0 | 0.0 |
| Max | 535.3 | 80.9 | 12.0 | 22.9 |
| Mean | 376.0 | 32.5 | 4.7 | 4.4 |
| Median | 396.7 | 32.1 | 4.4 | 4.7 |
| Stand.Dev. | 84.3 | 11.2 | 1.7 | 1.7 |
| CV% | 22.4 | 34.5 | 36.2 | 38.6 |

**Table 1**
*Descriptive statistics of the γ-ray data measured by "The Mole" (n = 23,854)*

The correlation coefficients between TC and radionuclides were low, except for the correlation between TC and $^{232}Th$ (fig. 2). In this case, Spearman rank order correlation coefficient (Rs) was high (0.74, $p < 0.0001$).

The values of radionuclides did not show strong differences among the four studied areas, whereas TC were, on average, higher in *DAT* and lower in *UMM* and *SAM*. *SAL* provided medium TC, with a median of 410 counts $sec^{-1}$. *UMM* showed the highest variance, with values between the first and third quartiles that spanned between 155 and 440 counts $sec^{-1}$. *SAL* and *SAM* showed higher homogeneity in terms of TC.

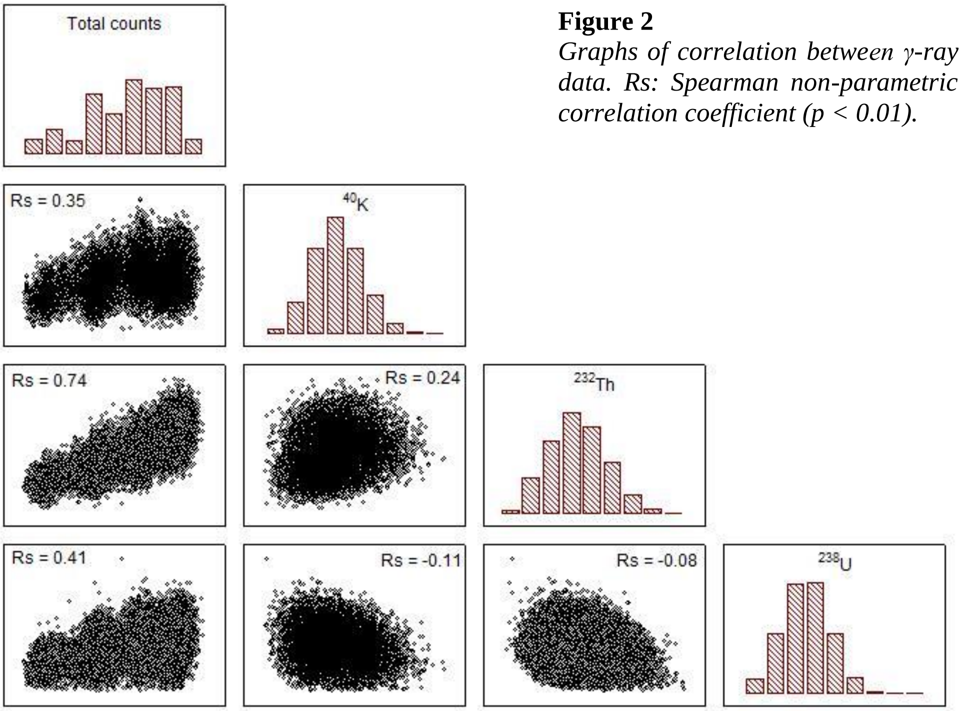

**Figure 2**
*Graphs of correlation between γ-ray data. Rs: Spearman non-parametric correlation coefficient ($p < 0.01$).*

The soils of the studied fields looked very similar in terms of texture, common vertic properties, presence of secondary carbonates and organic matter. The gravel content was very variable, also within the same field.

The 55 soil samples showed always a clayey texture (Tab. 2), with the only exception of a sample with sandy clay loam texture. Calcium carbonate had mean values between 15 and 22 g 100 $g^{-1}$ in the areas UMM, SAL and SAM, whereas lower values in DAT (0 to 5 g 100 $g^{-1}$). The mean values of total organic carbon (TOC) within the studied areas varied between 0.85-0.93 g 100 $g^{-1}$ in DAT and SAM, whereas was a little bit higher in UMM and SAL (1.35-1.43 g 100 $g^{-1}$). Total nitrogen (N) followed the pattern of TOC, with higher values in UMM and SAL (means = 0.14-0.16 g 100$g^{-1}$) and lower in DAT and SAM (means = 0.10-0.12 g 100$g^{-1}$).

| | Sand | Silt | Clay | $CaCO_3$ | TOC | N | Moisture* |
|---|---|---|---|---|---|---|---|
| | | | | g 100 $g^{-1}$ | | | |
| Min | 6.0 | 3.0 | 33.0 | 0.0 | 0.1 | 0.06 | 9.4 |
| Max | 50.0 | 35.0 | 77.0 | 41.5 | 1.97 | 0.26 | 24.0 |
| Mean | 17.0 | 21.8 | 61.3 | 16.0 | 1.1 | 0.13 | 18.3 |
| Median | 14.0 | 22.0 | 64.0 | 1.0 | 19.9 | 0.13 | 19.0 |
| Stand.Dev. | 10.3 | 6.5 | 10.1 | 11.8 | 0.4 | 0.03 | 3.1 |
| CV% | 60.6 | 29.7 | 16.5 | 74.0 | 31.3 | 25.0 | 16.9 |

**Table 2**
*Descriptive statistics of the soil samples (n= 55; * for moisture n=110).*

The correlation between soil features and γ-ray data showed significant correlations ($p < 0.01$) in most of the cases. The highest correlation, both parametric and non-parametric, was between clay content, TC and $^{232}$Th (Fig. 3; Tab. 3). High inverse correlations were also between sand, TC, $^{232}$Th and $^{40}$K. Calcium carbonate showed a significant direct correlation with $^{238}$U and significant inverse correlation with TC and $^{232}$Th (Fig. 3; Tab. 3).

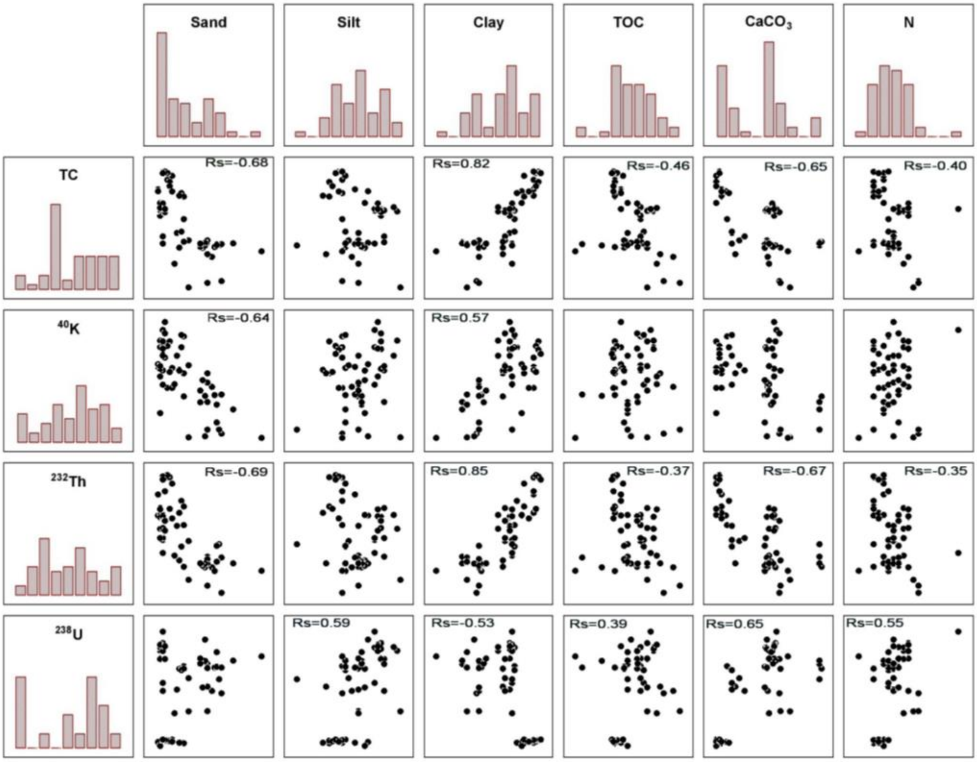

**Figure 3 -** *Scatterplot matrix between γ-ray and soil data of the experimental fields (N= 55). Rs: Spearman correlation coefficient for $p < 0.01$.*

| | Sand | Silt | Clay | CaCO3 | TOC | N |
|---|---|---|---|---|---|---|
| **Total counts** | **-0.68** | -017 | **0.80** | **-0.64** | **-0.39** | -0.33 |
| | **p<.001** | p=.215 | **p<.001** | **p<.001** | **p<.001** | p=.015 |
| **$^{40}$K** | **-0.71** | 0.15 | **0.63** | **-0.41** | 0.05 | 0.09 |
| | **p<.001** | p=.278 | **p<.001** | **p<.001** | p=0.72 | p=0.49 |
| **$^{232}$Th** | **-0.70** | -0.18 | **0.83** | **-0.68** | -0.32 | -0.35 |
| | **p<.001** | p=.191 | **p<.001** | **p<.001** | p=.017 | p=.010 |
| **$^{238}$U** | 0.25 | **0.52** | **-0.58** | **0.71** | 0.30 | **0.49** |
| | p=.067 | **p<.001** | **p<.001** | **p<.001** | p=.025 | **p<.001** |

**Table 3** *Pearson's correlations between γ-ray and soil data (N= 55). In bold $p < 0.01$.*

Total organic carbon (TOC) and nitrogen content showed lower but significant inverse correlations with TC and $^{232}$Th. Nitrogen showed significant direct correlation with $^{238}$U. In general, the non-parametric approach slightly increased the correlation coefficients.

The relationships between soil features and γ-ray data strongly varied in each area, showing low and not significant correlation coefficients in *SAL* and *SAM* areas, and very high correlation coefficients in *UMM*. In this area, Rs between clay and $^{232}$Th was 0.82 ($p < 0.01$), between $CaCO_3$ and TC was -0.85 ($p < 0.01$), between TOC and TC was -0.71 ($p < 0.01$). The correlation coefficients in DAT showed high significance only for clay (Rs = 0.64, $p < 0.01$).

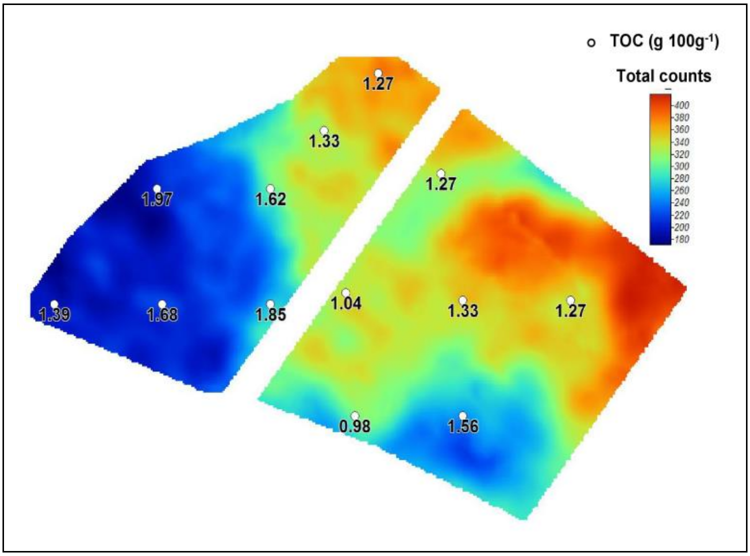

**Figure 4**
*Maps of TC (counts sec$^{-1}$), interpolated by ordinary kriging, in the UMM fields. White dots individuate the sampling points and the measured TOC. Spearman correlation coefficient between TOC and TC in the area UMM was significant (Rs= -0.71, $p < 0.01$).*

## Conclusions

The results of this work demonstrate the potentiality of γ-spectrometry for high detailed soil mapping, providing preliminary results about general correlations between several soil features and γ-ray data. The general correlations seem very promising for clay and calcium carbonate. A general predictive model of clay and calcium carbonate content for this kind of soils, namely clayey soils with vertic properties seems to be suitable. The correlation coefficients between soil features and γ-ray data decrease for sand, silt, TOC and nitrogen. For the prediction of these soil parameters by γ-ray data seems to be necessary a site-specific calibration.

Pre-processing of γ-ray data must be done, including the correction for soil moisture content. Future improvements of this innovative method should be done, taking in account other important soil features for γ-rays attenuation as bulk density (Beamish, 2013) and stoniness.

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