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PHYSICO-CHEMICAL CHARACTERIZATION OF SOIL SAMPLES FROM BÂRLAD MUNICIPALITY

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ABSTRACT

Soil quality is now thought of in a way that emphasises functionality in a broad context, involving soil not only as an environment for crop production but also as an important reservoir for water storage, as a buffer for filtering, transforming, and neutralising pollutants, and as a habitat for plants and animals. Some attributes (pH, soil conductivity, etc.) can be associated with several easily identified threats to soil quality, some of which are interrelated in the same way. For the present work, laboratory analyses were carried out to determine the physico-chemical parameters of soil from different areas. For soil quality analysis, the following parameters were determined: pH, conductivity, acidity, alkalinity, total nitrogen, aluminium, phosphates, iron, heavy metals, calcium, and magnesium content in the soil.

KEYWORDS: aqueous soil extract, acidity, alkalinity, heavy metal

1. Introduction

The continuous growth of the population requires the highest quality and highest possible agricultural production. Some of the measures that can lead to increased agricultural production are those that increase production per unit area and those that bring unproductive land into agricultural use. Solving these problems is based first and foremost on a thorough knowledge of the soil as the main means of agricultural production [1, 2].

As agriculture is the main source of food for a growing world population, the sustainability of agricultural production is a problem of great concern for the human race.

More attention is now being paid to increasing the country’s arable land area through the cultivation of new land and to preventing and combating soil pollution resulting from various anthropogenic activities (industrial, agricultural, etc.) [1].

Climate change is also expected to increasingly affect Romania and its agricultural sector in the medium and long term. Romania will have to expect a steady increase in average annual temperature, similar to projections for Europe, which can vary between 0.5 °C and 1.5 °C by 2029 and between 2.0 °C and 5.0 °C by 2099, depending on the global scenario. Precipitation patterns are expected to change significantly and have a differentiated territorial impact in Romania. The northern part of the country is likely to see gains in crop productivity in the medium term but will be subject to high winter rainfall and water shortage problems in summer. Southern and south-eastern Romania will be more severely affected and heat waves and droughts will lead to a general decrease in crop production and productivity [4].

Soil acidity is determined by dissociated H+ cations in water or saline solutions upon contact with the solid phase (actual or dissociated acidity) and by H^+ and Al^{3+} cations adsorbed on the surface of colloidal particles (potential or adsorbed acidity). Soil acidity controls the solubility and precipitation of the chemical compounds of all essential plant nutrients and is therefore a decisive factor in their availability.

Understanding the nature of soil acidity and managing it is an integral part of soil fertility. Soil acidity has a widespread influence on soil fertility and plant growth. For example, in strongly acid soils (pH < 5) Ca, Mg, P, B, and Mo become deficient, while Mn and Fe can reach toxic limits. Aluminium toxicity is also a serious problem for these soils. Similarly, the availability of Cu, Fe, Zn, and Mn is reduced in calcareous alkaline soils. In mineral soils, the pH for the highest availability of most nutrients is 6.5, while in organic soils (peat and mud) the optimum pH is around 5.5. For soils in our country, pH values range from 3.5 to 9.5 or 10-11 in the case of solonetz or sodic solonchak [1-3].

In addition, the pH affects the solubility and effectiveness of certain toxic chemicals (such as aluminium) and plants can absorb them [5].

The soil's pH has a direct association with the bacterial community in the ecosystem, which has a direct effect on soil acidification. Most microorganisms have an optimal pH range for survival and functioning [6].

A strong acidic or alkaline pH, due to the weak activities of bacteria-bound microbes determine the mineralisation of organic matter in the soil to slow down or stop. As a result, certain diseases will increase under conditions of low soil pH (acidic) or high soil pH (alkaline) [7].

Bacterial diversity and microbial activity are increased at higher pH values and decreased at lower soil pH values. Therefore, pH is a good predictor of bacterial community structure. Some environmental factors that define soil pH are mineral concentrations, erosion, mineralogy, and water balance [8-13].

Soil alkalinity can be natural or caused by human activity. Natural alkalinity is the result of the release of Na_2CO_3 from the soil through watering, while anthropogenic alkalinity, caused by human activities, is due to the application of fertilisers and irrigation water with high $NaHCO_3$ content [2].

Alhagi camelorum is a perennial plant widely distributed in Asia, Europe, America, and Australia, with reported uses in pharmaceuticals, animal feed and soil conservation. Alhagi may be a good indicator of soil alkalinity and could be considered a sign of low alkalinity and low salinity of soils in arid and rigid terrestrial ecosystems [14].

Plants take up calcium and magnesium in the form of Ca^{2+} and Mg^{2+}, available cations in most soils, although Mg deficiency is more common than Ca deficiency. Like calcium, magnesium can be easily leached and soils with low cation exchange capacity have low magnesium content. It is important that there is a balance of Mg, K, and Ca ions in the soil because these elements are dominant in areas with high cation exchange capacity. Since most soils with a pH of 7.0 or higher have abundant Ca and even Mg, it is generally not necessary to add these nutrients to crops each season [2, 3].

For example, chemical remedies could be used to alter the composition of cations adsorbed by soil aggregates. This would promote the formation of aggregate structures, improve soil structures and delay the return of soil salinisation. The most effective way to ensure the survival and sustainability of plant communities is to grow salt-tolerant halophytes [20].

In this study, determinations were performed for three types of soil taken from a depth of 10 cm: soil taken from a field in the area of Bârlad (Sample 1-P1), soil taken from the vicinity of the bearing factory in Bârlad (Sample 2- P2), and a garden soil sample taken from the area of Bârlad (Sample 3-P3).

For soil quality analysis, the following parameters were determined: pH, conductivity, acidity, alkalinity, total nitrogen, aluminium, phosphates, iron, heavy metal, calcium, and magnesium content in the soil.

To carry out the laboratory analyses, it was necessary to obtain an aqueous soil extract in a ratio of 1:5 by mixing 100 g soil with 500 mL distilled water. The mixture was stirred for one hour at medium speed for homogenization. After the stirring was completed, the aqueous soil extract was filtered through filter paper. The filtration operation is repeated as often as necessary to obtain a clear extract as possible for the next step, i.e. the above-mentioned analyses.

2. Results and discussions

Determining the soil's pH

The pH is the concentration of hydrogen ions in a solution, and the pH scale ranging from 0 to 14 units is used to measure the acidic and basic character of the solution. The natural pH of soil depends on the rock from which the soil was formed (base material) and the weathering processes that have acted on it – for example, climate, vegetation, topography, and time. These processes tend to cause a decrease in pH (increase in acidity) over time. Some agricultural activities can also accelerate the acidification process.

There are several methods to determine soil pH, but a portable HACH Multiparameter was used to monitor the pH of the aqueous soil extract in our field of interest.

Figure 1 shows the results obtained from the pH determination of aqueous soil extract.

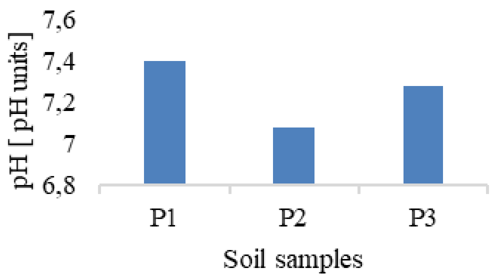

Fig. 1. *Results obtained after determining the pH of the aqueous soil extract*

It can be seen from the attached chart that the analysed soil has close pH values ranging from the lowest value of 7.08, which is the soil near the bearing factory, to a value of 7.4 pH units, which is

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the field soil. From these determinations, it can be concluded that the soil closest to neutral pH is sample 2.

The soil's reaction (soil pH) is of particular importance for the general characterization of soils, as well as for agricultural practice. It depends on the supply of nutrients to the soil.

Determining the soil's conductivity

Conductivity (also known as electrical conductivity or EC for short) is a measure of the ability of a substance to conduct an electric current and can be measured using a conductivity meter. In the agriculture and farming industry, conductivity can be used as an indicator of general soil nutrient levels.

The higher the conductivity and the concentration of salts, and the lower the conductivity, the easier it is to fertilize the soil. For this reason, it is necessary to analyse how electrical conductivity can affect substances in the soil.

During the determinations in the present study, the electrical conductivity of the soil was determined with the HACH portable Multiparameter.

According to the Commission Decision (EU) 2015/2099 of November 18, 2015, establishing the ecological criteria for the award of the EU Ecolabel for growing media, soil improvers and mulches, the electrical conductivity of the finished product must be less than 1000 µS/cm.

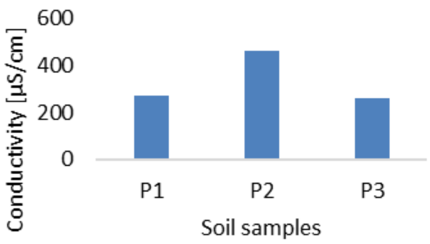

***Fig. 2.** Results obtained following the determination of soil conductivity*

In the attached chart in Figure 2, it can be seen that sample 2 has the highest electrical conductivity (465 µS/cm) and the other two soil samples have close values of electrical conductivity. None of the analysed soil samples exceeds the maximum value allowed by law.

Determining the soil's acidity

Hydrolytic acidity (A_h) is revealed by treating the soil with an alkali-hydrolysing salt (consisting of a strong base and a weak acid), which removes more adsorbed hydrogen or other acidic ions.

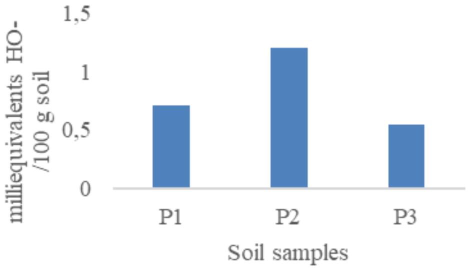

***Fig. 3.** Results obtained following the determination of soil acidity*

As can be seen from the above chart, the soil sample with the highest acidity is sample 2, followed by sample 1, and the lowest value was obtained from the soil sample taken from the garden (sample 3).

Hydrolytic acidity is the parameter that really indicates the quality of soil. When analysing soil, a number of parameters can fluctuate depending on the moisture level, but hydrolytic acidity is a constant that indicates the physical and chemical state of the soil at any given time. Experts have explained that a hydrolytic acidity level between 0 and 1 indicates soil with a good pH.

Determining the soil's total alkalinity

The alkaline reaction of the soil solution is determined by the composition of different compounds in the soil: carbonates in alkaline and alkaline-earth bicarbonates, sodium silicates, sodium humates, etc. Soil alkalinity can be natural or caused by human activity. Natural alkalinity is the result of the release of Na_2CO_3 from the soil by watering the soil, while artificial alkalinity, caused by human activities, is due to the application of fertilizers and irrigation water with high $NaHCO_3$ content [1].

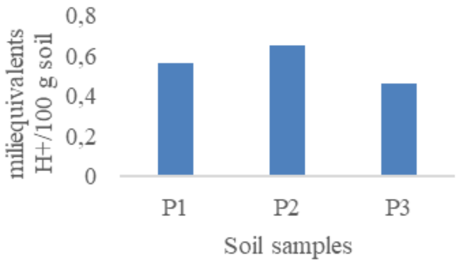

***Fig. 4.** Results obtained following the determination of soil alkalinity*

The chart presented in Figure 4 shows that the soil sample with the highest alkalinity is sample 2, with alkalinity of 0.651 milli equivalents H^+/100 g soil followed by the other samples with similar values. All analysed soil samples are weak in alkaline.

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Determining the calcium and magnesium cation content

The soil solution contains mineral, organic, and organo-mineral combinations. The mineral compounds consist of salts of mineral acids (carbonates, bicarbonates, ammonium, nitrates, nitrites, chlorides, sulphates, phosphates of Ca, Mg, Na, K, etc.) and various acids of Fe, Al, Mn. Organo-mineral combinations with different degrees of solubility are formed by combining humic acids with other types of organic acids with basic ions, represented by Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, etc. Calcium and magnesium cations in the soil are intended to improve the physical, chemical, and biological characteristics of the soil, correct over-acidification, and reduce soil depletion. Ca and Mg salts help restore soil structure [1].

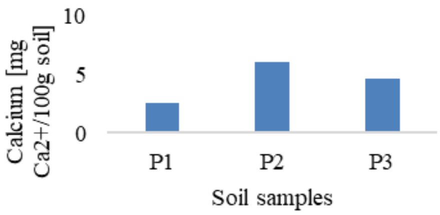

***Fig. 5.** Results obtained following the determination of calcium content*

The importance of calcium in soil is essential for healthy crops, especially if you grow vegetables. Calcium regulates the acid balance, but if the macronutrient is not sufficient, the concentration of acid in the soil starts to increase, disrupting root nutrition.

From the data presented in Figure 5, we can observe a difference between the soil sample from the field (sample 1) with the lowest value (2.52 mg Ca^{2+}/100 g sol) and soil sample 2 which has the highest value for calcium content (6.048 mg Ca^{2+}/100 g sol). The garden sample (soil sample 3) has a medium calcium content comparing the two extreme values.

The signs of a calcium deficiency in the soil are visible in crop plants: stunted growth, chlorosis, brown leaf tips, and spots. These tell you when the soil is suffering from a lack of calcium and when to intervene to lower the soil pH level when the soil has become too acidic.

The graph represented in Figure 6 shows a low magnesium content obtained in the garden soil sample (sample 3), the highest value for soil magnesium content was obtained for sample 2, 14.7 mg Mg^{2+}/100 g soil.

The main symptom of magnesium deficiency in plants is interveinal chlorosis. Interveinal chlorosis occurs when a yellow discoloration, sometimes accompanied by a reddish-brown colour appears between the leaf veins. The veins themselves remain green. The key to identify a magnesium deficiency is the localization of this chlorosis, as it can be mistaken for iron deficiency.

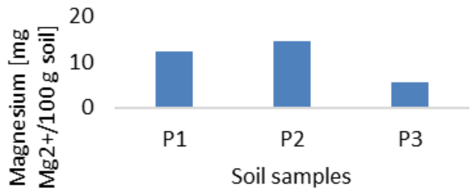

***Fig. 6.** Results obtained following the determination of magnesium content*

Determining the total nitrogen in soils

Nitrogen is one of the major elements necessary for life. It will simulate above-ground growth and produce the rich green colour that is characteristic of healthy plants, which is why nitrogen is essential for the plant's life. 78% of the atmosphere is covered by molecular nitrogen (N_2); Total nitrogen determination was carried out using a UV-VIS DR 5000 spectrophotometer with special standard solutions to identify the total nitrogen content in the soil.

Figure 7 shows the spectrophotometer used in some of the analyses carried out for this study.

***Fig. 7.** Spectrophotometer HACH LANGE DR5000*

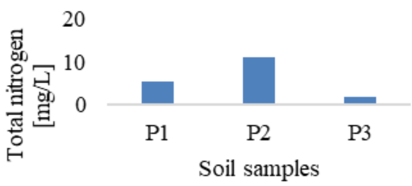

***Fig. 8.** Results obtained following the determination of total nitrogen*

From the graph presented in Figure 8, we observe that the highest total nitrogen content was obtained in soil sample 2, followed by the field soil

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sample (sample 1) and the lowest total nitrogen content in soil was obtained for the garden soil sample (sample 3).

Determining the aluminium content in the soil

The determination of the aluminium content in the aqueous soil extract was carried out using the UV-VIS DR 5000 spectrophotometer at a wavelength of 620 nm.

Fig. 9. *Aluminium determination kit*

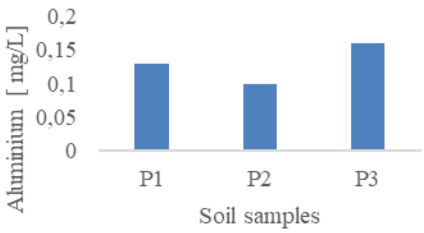

Fig. 10. *Results obtained following the determination of aluminium*

According to the above graph, the highest amount of aluminium was found in the garden soil sample (sample 3), i.e. 0.16 mg/L, followed by the field sample with a close value of 0.13 mg/L, and the lowest amount of aluminium was found in sample 2, i.e. 0.10 mg/L.

Soil aluminium test results provide suggestions for correcting soil toxicity, one of the best ways to correct soil toxicity is agricultural lime.

Determination of phosphates

Phosphates are found in the soil as easily soluble primary phosphates and as secondary phosphates, tertiary, ortho-alkalcic phosphates, phosphates adsorbed on the surface of iron and aluminium oxides, or clay, which are poorly soluble.

The determination of phosphates in the aqueous soil extract was carried out by spectrophotometer and had the following steps: the foil from the cap of the bottle was removed with the standard solution, 2 mL of the sample was pipetted to be analysed, then the cap with the inner part was put to mix with the substance in the stopper and vigorously shook; then heated in a thermostat for one hour at 100 °C; the vial was allowed to cool to room temperature, then shook rigorously several times, then added 0.2 mL of reagent B, stirred several times and inserted into the spectrophotometer for reading the result.

Fig. 11. *Phosphate determination kit*

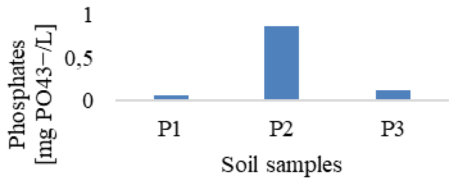

Fig. 12. *Results obtained following the determination of phosphates*

As can be seen in the graph above, the highest number of phosphates was detected in sample 2 with a value of 0.87 mg PO_4^{3-}/L, the other two samples being close in terms of values, the lowest being for sample 1 with 0.058 mg PO_4^{3-}/L.

According to studies, the factors influencing phosphorus retention in soils are: soil pH, soil texture and structure (clay-rich soils contain high amounts of phosphorus), iron, aluminium, calcium, and magnesium content, soil moisture and temperature.

Determination of iron

To determine the iron content in the sample to be analysed, it was proceeded as follows: 2 mL of the aqueous extract sample was pipetted into a vial containing the standard solution, then the vial was closed and homogenized the content. After a 5-minute pause, it was shaken a few more times, then the vial was placed in the spectrophotometer cuvette to determine the iron content.

The graph presented in Figure 13 shows that the highest value for iron content is obtained for soil sample 2 with a value of 0.895 mg Fe^{2+}/Fe^{3+}/L, the lowest value being identified in soil sample 3 from the garden, i.e. 0.489 mg Fe^{2+}/Fe^{3+}/L.

In iron excess, the leaves are initially covered with browning spots which with time turn a uniform

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brown colour. Excess iron occurs on acid soils and excess moisture, where the soluble Fe content can increase from 0.1 to 50-100 ppm in only a few weeks.

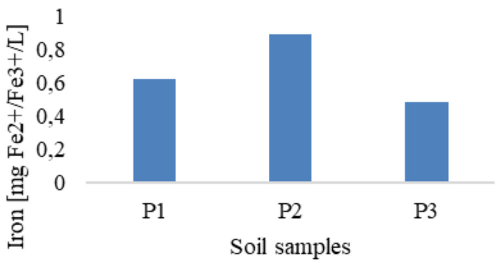

Fig. 13. *Results obtained after determining the iron content*

Determining heavy metals in the soil

Heavy metals fall into two categories: essential and non-essential.

Essential metals (micronutrients) are: chromium, cobalt, copper, manganese, molybdenum, iron, selenium, and zinc, which are necessary for the optimal functioning of biological and biochemical processes in the body.

Non-essential metals such as arsenic, cadmium, mercury, and lead have no known biological function.

The determination of the amounts of metals was carried out using the X-ray fluorescence spectrometer. X-ray fluorescence spectroscopy (XRF) measures the characteristic X-rays emitted from a sample after it is bombarded with high-energy radiation.

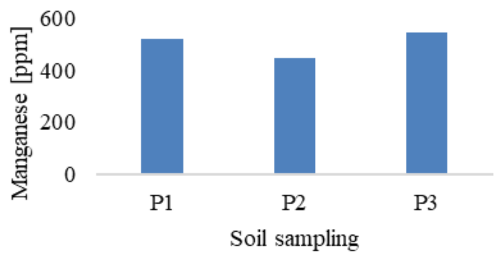

Fig. 14. *Results obtained following the determination of manganese content*

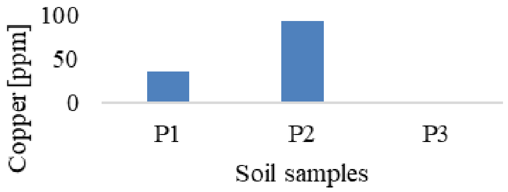

Fig. 15. *Results obtained following the determination of copper content*

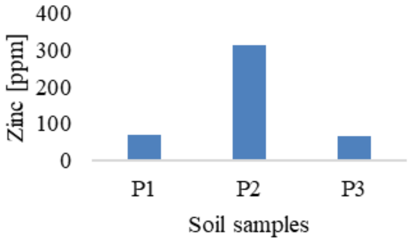

Fig. 16. *Results obtained following the determination of zinc content*

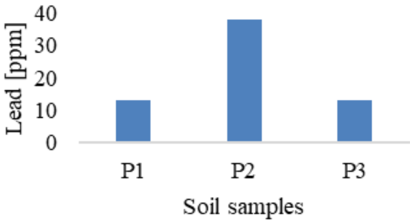

Fig. 17. *Results obtained following the determination of lead content*

From the data presented in Figures 14-17, the following can be observed:

The amount of manganese is relatively equal for all analysed soil samples, around 450 ppm, which means that it is within the values required by the legislation, the normal values being 900 mg/kg dry soil.

Concerning the amount of copper in the analysed soil samples, it was detected only in two of the three samples, i.e. sample 2 and sample 1, values above the normal value were detected, respectively 36 ppm and 94 ppm, the threshold of the normal value being 20 mg/kg, but below the alert threshold, which is 100 mg/kg dry soil.

Zinc is found in all analysed soil samples with values close to each other for the garden and field samples, around 70 ppm, but a higher value was obtained for sample 2, i.e. 312 ppm slightly above the alert threshold (AT alert threshold – 300 mg/kg dry soil).

As in the municipality of Bârlad, the nearby area where the zinc concentration exceeds the alert threshold is an industrial zone, it is possible that this is one of the determining factors of zinc concentrations above the alert threshold value.

The concentration of lead in the reference areas is approximately the same for the garden and field samples, i.e. around 13 ppm, but for soil sample 2 a higher value of 38 ppm was detected, above the normal value (20 mg/kg dry soil) but still below the alert threshold (50 mg/kg dry soil).

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3. Conclusions

Soil is a complex environmental factor without which life on Earth would not be possible. Due to the constituents that are often found in soil (mineral and organic matter, air, water, and micro-organisms) and with the help of which soil fulfils certain functions such as water purification, nutrient recycling and gas exchange with the atmosphere. Since the soils analysed in this article do not have an ideal composition, changes in the content of soil phases will influence the physical, chemical, and biological properties of the soil.

The study of the soil in the sampling areas consists of laboratory analysis in order to determine the soil quality. The soil has been analysed in terms of physico-chemical parameters by the following determinations: pH, conductivity, acidity, alkalinity, total nitrogen, aluminium, phosphates, iron, heavy metals, calcium, and magnesium content in the soil.

The results obtained from the soil pH determination – show that all samples have a pH close to neutral to weakly alkaline with values between 7-7.4 pH units.

Determination of soil alkalinity – the highest alkalinity was obtained for soil sample 2 with an alkalinity of 0.651 milli equivalents H^+/100 g soil, followed by the other two samples with values close to each other. All analysed soil samples are weakly alkaline.

Soil acidity determination – the highest soil acidity value was obtained for soil sample 2, followed by soil sample 1, and the lowest value was obtained from soil sample 3.

Determination of heavy metals content in soil – regarding the amount of copper in the analysed soil samples, values above the normal value were detected, i.e. 36 ppm in soil sample 1 and 94 ppm in soil sample 2, the threshold of normal value was 20 mg/kg, but below the alert threshold.

Zinc is found in all analysed soil samples with values close to each other for the garden and field samples, around 70 ppm, but a higher value was obtained for soil sample 2, i.e. 312 ppm slightly above the alert threshold.

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