

Soil Fertility in Coal Sterile Dump Assessment in Jiu Valley - Romania

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ABSTRACT: Coal mining results in large quantities of sterile material that are deposited in dumps. In Jiu Valley, there are over 40 sterile dumps that are mostly not revegetated. These facts represent the main environmental impact in the area. In order to develop other activities, including tourism, simultaneously with mining activity reduction, it is necessary to lessen this soil and visual impact. Revegetation represents the only permissible solution, but this activity must take into account the existing ecological structure. The main issue is the soil regeneration. This process is very complex, and for this reason it is very difficult to assess fertility increase. Different species of plants grow differently in the same conditions, so it is not possible to evaluate soil fertility by vegetal production. Our systematic studies of sterile dumps allow us to draw the conclusion that chemical parameters like humic acids, nitrites and phosphates do not correlate well with soil fertility. To complete the soil fertility evaluation, we introduce other enzymatic analyses, including urease, invertase and catalase, which offer us more information about fertility. These results correlated with the chemical composition, allowing us to better assess the soil fertility and suitability for revegetation.

1 INTRODUCTION

Technogenic soils are soils that are formed after re-cultivation of mining waste dumps. These wastes are also a hazardous source of pollution in the environment.

The evolution of technogenic soils is defined like waste transformation into agricultural or forestry soils. Simultaneously, these processes take place together with the reducing or removing of pollutants. These processes are very important because mining activity results in ever-greater amounts of waste from one year to the next. It is estimated that in the world there is over 1600 billion cubic meters of waste in dumps and that that volume increases every year by

40 billion cubic meters. In comparison, land affected by erosion is estimated to amount to 13 billion cubic meters per year. According to some estimations, for every million tonnes of coal mining, in Romania 40-50 hectares of fertile soil is affected.

Technogenic soil evolution is also important also with regard to the landscape.

Technogenic soil evolution reflects revegetation efficiency. Technogenic soil evolution may be assessed by different methods: physical, chemical and biological. In some countries like Russia, the Ukraine and the U.S.A., enzymological methods have been reported. In this study, we consider ten different soils in some mining areas in Jiu Valley, Romania (Table 1).

Table 1. Soil samples considered in this study.

Sample	Place	Characterisation
1	Petrila Mine - natural soil	vegetated poor soil
2	Petrila Mine - dump	un vegetated soil
3	Aninoasa Mine - Tericom Dump	very poor vegetated soil
4	Aninoasa Mine - natural soil close to Tericom	poor vegetated soil
5	Petrila Coal Processing Plant- natural soil	vegetated soil
6	Livezeni Mine - PAJ dump	very poor vegetated soil
7	Aninoasa Mine - Pisu dump	well revegetated dump
8	Aninoasa Mine - natural soil	vegetated soil
9	South Aninoasa Mine - natural soil	vegetated soil
10	North Aninoasa Mine - natural soil	vegetated soil

2 SOIL FERTILITY ASSESSMENT

2.1 Phosphorus

Although the percentage of phosphorus in plant material is relatively low, it is an essential component of plants. Phosphorus, like nitrogen, must be present in a simple inorganic form before it can be taken up by plants. In the case of phosphorus, the utilisable species is some form of orthophosphate ion. In the pH range that is present in most soils, H_2PO_4^- and HPO_4^{2-} are the predominant orthophosphate species.

Orthophosphate is most available to plants at pH values near neutrality. It is believed that in relatively acidic soils, orthophosphate ions are precipitated or sorbed by species of Al(III) and Fe(II). In alkaline soils, orthophosphate may react with calcium carbonate to form relatively insoluble hydroxyapatite.

Generally, because of sorption and precipitation, little phosphorus applied as fertilizer leaches from the soil. This is important from in view of both water pollution and utilisation of phosphate fertilizers.

2.2 Potassium

Relatively high levels of potassium are utilized by growing plants. Potassium activates some enzymes and plays a role in the water balance in plants. It is also essential for some carbohydrate transformations. Crop yields are generally greatly reduced in potassium-deficient soils. The higher the productivity of the crop, the more potassium is removed from soil. When nitrogen fertilizers are added to soil increase productivity, removal of potassium is enhanced. Therefore, potassium may become a limiting nutrient in soils heavily fertilized with other nutrients.

Although potassium is one of the most abundant elements in the Earth's crust, of which it makes up 2.6%, much of this potassium is not easily available to plants. For example, some silicate minerals such as leucite, $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$, contain strongly bound potassium. Exchangeable potassium held by clay minerals is relatively more available to plants.

2.3 Nitrogen

Nitrogen is an essential component of proteins and other constituents of living matter. Plants and cereals grown on nitrogen-rich soils not only provide higher yields, but are often substantially richer in protein and, therefore, are more nutritious. Nitrogen is most generally available to plants as nitrate ion, NO_3^- . Some plants such as rice may utilise ammonium nitrogen; however, this form of nitrogen poisons other plants. When nitrogen is applied to soils in the ammonium form, nitrifying bacteria perform an essential function in converting it to available nitrate ion.

Nitrogen fixation is the process by which atmospheric N_2 is converted to nitrogen compounds available to plants. Human activities are resulting in the fixation of a great deal more nitrogen than would otherwise be the case. Artificial sources now account for 30-40% of all nitrogen fixed. These include chemical fertilizer manufacture; nitrogen fixed during fuel combustion; combustion of nitrogen-containing fuels; and the increased cultivation of nitrogen-fixing legumes. A concern with this increased fixation of nitrogen is the possible effect upon the atmospheric ozone layer by N_2O released during denitrification of fixed nitrogen.

Prior to the widespread introduction of nitrogen fertilizers, soil nitrogen was provided primarily by legumes. These plants, such as soybeans, alfalfa, and clover, contain in their root structures bacteria capable of fixing atmospheric nitrogen. Leguminous plants have a symbiotic (mutually advantageous) relationship with the bacteria that provide their nitrogen. Legumes may add significant quantities of nitrogen to soil, up to 10 pounds per acre per year, which is comparable to amounts commonly added as synthetic fertilizers. Soil fertility with respect to nitrogen may be maintained by rotating plantings of nitrogen-consuming plants with plantings of legumes, a fact recognised by agriculturists as far back as the Roman era.

The nitrogen-fixing bacteria in legumes exist in special structures in the roots called root nodules. The rod-shaped bacteria that fix nitrogen are members of a special genus called *Rhizobium*. These bacteria may exist independently, but cannot fix nitrogen except in symbiotic combination with plants. Although all species of *Rhizobium* appear to be very similar, they exhibit a great deal of specificity in their choice of host plants. Curiously, legume root nodules also contain a form of hemoglobin, which is apparently involved in the nitrogen-fixation process.

In Table 2, the main soil nutrient element content is presented.

2.4 Soil Porosity

Soil particle size largely determines the physical character of soil. Classified according to size, clays consist of particles smaller than 0.002 mm, while silt particles are 0.002-0.05 mm, sand is 0.05-1 mm, and gravel exceeds 1 mm. Soil texture is classified according to relative amounts of clay, silt, and sand. One of the more productive kinds of soils is loam, which consists of approximately 40 percent silt, 40 percent sand, and 20 percent clay. Even better for agricultural purposes is sandy loam, which is typically 70% sand, 10% clay, and 20% silt.

Table 2. The main soil nutrient element content.

Sample	Humus	assimilable N	assimilable P	assimilable K
1	16.5	0.85	16.2	23.6
2	0	0	0.6	5.8
3	2.5	0.10	0.15	2.15
4	13.4	0.69	12.12	8.20
5	14.8	0.51	14.7	12.1
6	0.5	0.12	0	2.35
7	1.8	0.05	0.25	2.25
8	17.5	0.91	13.6	7.9
9	12.3	0.78	15.60	14.35
10	10.5	0.75	16.30	8.9

Normally, because of the small size of soil particles and the presence of small capillaries and pores in the soil, the water phase is not totally independent of soil solid matter. Access of soil water to plants is governed by gradients arising from capillary and gravitational forces. The availability of nutrient solutes in water depends upon concentration gradients and electrical potential gradients. Water present in larger spaces in soil is relatively more available to plants and readily drains away. Water present in smaller pores, or between the unit layers of clay particles is held much more strongly. Soils high in organic matter may hold appreciably more water than other soils,

but it is relatively less available to plants because of physical and chemical sorption of the water by the organic matter.

There is a very strong interaction between clays and water in soil. Water is absorbed on the surfaces of clay particles. Because of the high surface/volume ratio of colloidal clay particles, a great deal of water

may be bound in this manner. Water is also held between the unit layers of expanding clays, such as the monmorillonite clays.

Roughly 35% of the volume of typical soil is composed of air-filled pores. Whereas the normal dry atmosphere at sea level contains 21% O₂ and 0.03% CO₂ by volume, these percentages may be quite different in soil air because of the decay of organic matter. This process consumes oxygen and produces CO₂. As a result, the oxygen content of air in soil may be as low as 15%, and the carbon dioxide content may be several percent. Thus, the decay of organic matter in soil increases the equilibrium level of dissolved CO₂ in ground water. This lowers the pH and contributes to weathering of carbonate minerals, particularly calcium carbonate. The presence of CO₂ also shifts the equilibrium of the process by which roots absorb metal ions from soil.

Table 3. Soil granulometry.

Sample	Large sand	Fine sand	Powder I	Powder II	Clay	Humidity
1	54.39	32.48	9.62	2.36	1.15	5.2
2	56.69	21.58	7.78	1.63	12.32	2.1
3	66.67	20.28	4.21	0.63	8.21	7.85
4	14.48	39.59	21.17	12.38	12.38	5.23
5	42.64	29.25	14.60	4.73	8.78	4.6
6	42.64	29.25	14.60	4.73	8.78	2.4
7	62.64	21.80	5.83	1.75	7.98	7.85
8	46.51	27.47	15.49	4.00	6.53	5.58
9	59.89	17.24	6.93	1.59	14.35	6.3
10	18.23	35.46	21.15	10.69	14.47	4.75

2,5 Acid-base and ion exchange reactions in soils

One of the more important chemical functions of soils is the exchange of cations. The ability of sediment or soil to exchange cations is expressed as the cation-exchanged capacity, the quantity of monovalent cations that can be exchanged per 100 g of soil. The cation-exchanged capacity varies with soil conditions such as pE and pH. Both the mineral and organic portion of soil exchange cations. Clay minerals exchange cations because of the presence of negatively-charged sites on the mineral, resulting from the substitution of an atom of lower oxidation number for one of higher number, like magnesium or aluminum. Organic materials exchange cations because of

the presence of the carboxylate group and other basic functional groups. Humus typically has a very high cation-exchange capacity.

Cation exchange in soil is the mechanism by which potassium, calcium, magnesium, and essential trace-level metals are made available to plants. When nutrient metal ions are taken up by plant roots, hydrogen ion is exchanged for the metal ions. This process, plus the leaching of calcium, magnesium and other metal ion from the soil by water containing carbonic acid, tends to make the soil acidic. Soil acts as a buffer and resists changes in pH. The buffering capacity depends upon the type of soil.

Acid-base and ion exchange reactions in the soils of the studied samples are shown in Table 4.

Table 4. Acid-base and ion exchange soil properties.

Sample	pH	cation-exchanged capacity	hydrogen-exchanged capacity	Total exchanged capacity
1	5.4	4.69	21.63	26.32
2	6.1	0.00	0.00	0.00
3	7.6	3.60	2.55	6.15
4	5.8	20.21	22.57	42.78
5	5.4	5.19	15.82	21.01
6	7.6	0	0.15	0.15
7	7.2	2.75	1.90	4.65
8	5.8	8.47	46.95	55.42
9	5.4	16.78	23.56	40.34
10	6.1	18.60	21.35	39.95

Tables 2-4 show that the physical and chemical properties are not well correlated with real characteristics, including the vegetation growing stage.

3 ENZYMATIC REACTIONS IN SOIL

3.1 Nitrogen Organic Compound Decay by Soil Microorganisms

In the soil there are important amounts of nitrogen organic compounds. They provide 99% of the total nitrogen reserves in the soil. However, large amounts of nitrogen compounds reach the soil every year from dead plants and animals. If this amount of nitrogen were fixed without any transformation, the nitrogen available for plants would decrease every year, making growth impossible. This does not happen because these compounds are decayed continuously in soil by the forming of simpler nitrogen organic compounds. These processes of nitrogen compound transformation into ammonia are known as ammonification processes. These processes are very important for natural life and agriculture.

Some bacteria produce urea decomposition:

1. *Bacillus probatus* is a great sporulate bacillus capable of decomposing up to 140 g urea per liter of nutritive solution. It is a widespread bacterium in nature. Similar activities occur in two more bacteria: *Urobacillus Leubii* and *Urobacillus Miquelii*, but they exhibit a lower level of activity than *Bacillus Probatus*.

2. *Planoscucina urea* are cocci from the mobile charges group that form small cubic heaps of 4-8 spherical cells. These bacteria are less active than the forms above, but they decompose up to 30 g urea per liter of nutritive solution.

3. *Micrococcus urea* is a spherical bacterium that decomposes urea relatively slowly.

Apart from these bacteria, there are other forms from the same group, very widespread in water basins, in lagoons, wetlands and other natural substrate. Some of them decompose relatively active urea, e.g. *Urobacteria hesmogenes* that can hydrolyse a 5% urea solution completely in 24 hours.

A characteristic feature of these bacteria is their ability to grow in a high alkaline reaction of nutritive substrate. The lowest pH that allows their growth is 7.0 and the optimal value is over 8.0. These characteristics of urobacteria are related to the

fact that they constantly release ammonia into their environment during vital activities, in this way producing a strongly alkaline reaction. During their phylogenetic evolution, these bacteria were adapted to this environment. The same conditions made these bacteria become more resistant to free ammonia. They easily resist ammonia solution of a few percent concentration, while the growth of other bacteria is interrupted even with low free ammonia concentrations in nutritive solution. The bacteria behaviour given by environmental redox potential is also very different. They may grow and reproduce, decomposing urea to rH values between 28 and 0.8, which means both aerobic and anaerobic conditions. For carbon sources, they may use the most different carbon compounds from soil, like organic acid salts, especially citric acid, maleic acid, succinic acid and acetylic acid as well as monosaccharides, disaccharides, dextrin and starch. Urobacteria use mainly organic acid salts that do not contain oxidised carbon (acetic and succinic acids). For nitrogen sources, they most easily use the ammonium salts and free ammonium that are formed as a result of urea hydrolysis. Although urea, in addition to nitrogen, contain carbon, they cannot use it because it is too oxidised, forming by hydrolysis carbon dioxide. For this reason, urea represent just a nitrogen source for bacteria. The urea decay mechanism is simple enough, being one of desamination:



The resulting ammonium carbonate is not very stable, and is decomposed to its component parts;



The desamination reaction is produced by an enzyme known as ureasis.

According to some authors, this enzyme is placed outside bacteria and the hydrolysis process itself has just an environmental role for bacteria. According to other authors, rapid urea decomposition takes place just in the presence of bacteria and not in the filtrate of their culture. This fact does not exclude the possibility that the urea decomposition process has a physiological role inside the cells.

For the soil samples we determined the ureasis activity and the results correlated very well with the existing situation (Table 5).

Table 5. Ureasis soil activity.

Sample	Ureasis activity mg NH ₄ ⁺ /24 hours
1	3.383
2	1.264
3	0.800
4	1.678
5	2.203
6	2.308
7	2.439
8	2.911
9	2.518
10	4.721

4 CONCLUSIONS

1. Chemical and physical analyses do not always reflect soil fertility characteristics. For different reasons, including microorganism activity, soils rich in nutrients may be poorly vegetated, and poor soils may be well vegetated.
2. Enzymological activity analysis matches better with vegetation development, because it takes into account the microorganism activity.
3. Enzymological analysis technology is very simple and does not require special laboratory equipment.

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