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ORIGINAL RESEARCH

Leachate fermentation from composting organic mineral liquid fertilizer: Effects on the behavior of phosphorus, potassium and organic acids

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Abstract

Purpose: Fermentation process could be a low-cost strategy to stabilize and transform liquid organic residues into organic fertilizers for agricultural use. However, low nitrogen (N), phosphorus (P) and potassium (K) levels have hampered its potential use as an organic fertilizer. So, this study investigated the behavior of P, K and organic acids in the fermentation of the leachate from urban organic solid waste (UOSW) enriched with phosphoric rock (PR) and K sulfate.

Method: Tests for obtaining liquid organic fertilizers rich in P and K were conducted using a 3×3 factorial experiment. The concentrations 5%, 10% and 15% PR, 2.5%, 5 and 10% K sulfate with fractions of the treacle, magnesium sulfate, urea, manganese sulfate, zinc and iron were used. The monitoring of the variables was conducted by using UV-Vis, atomic absorption and HPLC for organic acids.

Results: The concentrations of total phosphorus (TP) and K are influenced by the content of PR. However, the highest content of water-soluble phosphorus (W-SP) was observed in treatments containing 5% and 10% PR. Furthermore, the pH changes were related to the presence of short-chain organic acids. Finally, acetic acid (AA), lactic acid (LA), citric acid (CA), propionic acid (PA) and tartaric acid (TA) were identified as products of the decomposition of organic matter.

Conclusion: The use of leachate for the production of liquid fertilizers can reduce the amount of waste going to landfills and minimize environmental impact. Also, it can be used as a benefit for soil health by providing essential nutrients to plants.

Keywords: Leachate, Mineralized liquid fertilizer, Fermentation, Phosphoric rock

Introduction

One of the main challenges related to the stabilization of organic matter through composting is the production of leachate, which occurs due to the high water content (60% to 90%) present in organic waste (Roy et al. 2018). Leachates are characterized by a high concentration of organic matter, chemical oxygen demand (COD), salts, minerals and ammonia. If untreated leachates are discharged directly into the environment, they could contribute to eutrophication and directly impact water resources (Arora and Keshari, 2020; Hashemi et al., 2017; Postacchini et al., 2018). The amount of leachate depends on the composting process and the material being composted. For instance, municipal waste generates approximately 75-100 L of leachate per ton (Hashemi et al. 2017). In the municipality of Paipa (study site), approximately 241.25 Tn of urban organic solid waste (UOSW) and 4.11 Tn of rural organic solid waste are generated monthly, combining for a total of 245.36 Tn, which would correspond to approximately 13,500 liters of leachate produced per month (Alcaldía de Paipa 2020).

Over the years, it has been proposed that organic solid waste materials could be used for energy generation as methane gas production (Hassan et al. 2018; Selena-Mesías et al. 2022), production of industrially important organic substances as organic acids (Bhalla et al. 2012), or organic fertilizer (Ameen 2020; Chinga et al. 2020). Organic fertilizer use has gained momentum due to the high cost of fertilizer inputs and the depletion of natural resources such as highly soluble phosphoric rock (PR) (Panhwar et al. 2013). Studies have shown that leachates can increase the availability of nutrients such as P and K in soils. Organic matter content serves as food for microorganisms that facilitate the transformation of chemically unavailable species into available ones, such as $H_2PO_4^-$, HPO_4^{2-} or the K^+ ion (Tate 1992). Additionally, microbiological processes can generate organic species, such as acids, which promote plant growth and development by affecting P availability. This is achieved by reducing fixation processes that occur with Fe and Al in acidic soils and Ca in basic soils, as well as enhancing K mobility (Shen et al. 2023).

However, low levels of nutrients in the leachates have encouraged the search for alternative methods which can increase mineral concentration and produce a fertilizer that complies with the national standard (NTC 5167 2011) and has a greater impact on agricultural yields. In this sense, the liquid organic fertilizers with minerals (LOFM) produced by fermentation, are a strategy to improve soil health, as the final product contains nutrients such as NPK, phytohormones, organic acids, organic matter and microorganisms which can contribute to soil remediation, promote plant growth and enhance food production. For instance, Phibunwatthanawong and Riddech (2019) used leachate combined with different combinations of molasses, distillery waste and sugarcane leave to make organic fertilizers through fermentation. This was then used in the growth and development of Cos lettuce (*Lactuca sativa var. Longifolia*). Results showed comparable effects on lettuce growth and chlorophyll content compared to commercial fertilizer, despite the organic fertilizer's low NPK content. Thus, the objective of this study was to investigate the behavior of P, K and organic acids in leachate enriched with PR and K sulfate and treated by fermentation in UOSW from Paipa, Boyacá, Colombia.

Materials and methods

Leachates

Leachate was obtained from the public utility company Red Vital located in the municipality of Paipa, Boyacá, Colombia and transported in plastic containers to the Soil Laboratory of the Fundaciòn Universitaria Juan de Castellanos, located in the San Francisco de Asís Veterinary Clinic in Soracá, Boyacá, Colombia. Once at the laboratory, the leachate was enriched with sources of P, K, N and minerals such as Mg, Zn, Mn and Fe.

Production of mineralized liquid fertilizer rich in P and K

The tests for obtaining liquid organic fertilizers rich in P and K were conducted using a 3×3 factorial experiment arranged in a randomized design with three replications (See Apendix, Table 1. Experimental matrix of the 3×3 factorial design). The first factor was the concentration of PR by using three levels: 5%, 10% and 15%. The second factor was the concentration of K by using three levels: 2.5%, 5%, and 10%. In total, there were 10 treatments: T0 (leachate without the addition of minerals), T1 (PR 5%, K 2.5%), T2 (PR 5%, K 5%), T3 (PR 5%, K 10%), T4 (PR 10%, K 2.5%), T5 (PR 10%, K 5%), T6 (PR 10%, K 10%), T7 (PR 15%, K 2.5%), T8 (PR 15%, K 5%) and T9 (PR 15%, K 10%) (Fig. 1). The different tests for obtaining mineralized liquid fertilizer were conducted at the laboratory level in a 3 L container. 2.5 L of leachate were taken for each test and all combinations were enriched with 5% molasses, 5% magnesium sulfate, 5% urea, 0.5% manganese, 0.5% zinc, 0.5% iron sulfates and 0.5% boric acid. All samples were stirred once a day for 5 minutes to homogenize and oxygenate the system. Samples were collected every 5 days over a period of 15 days. The measured physicochemical variables included the behavior in organic acid production, total phosphorus (TP), soluble phosphorus (SP), pH, electrical conductivity (EC) and total minerals (K, N, C, Na, Mg, Mn, Zn, Fe and Ca). The latter were only analyzed on the 15th day. Microbiological variables were not considered in this study.

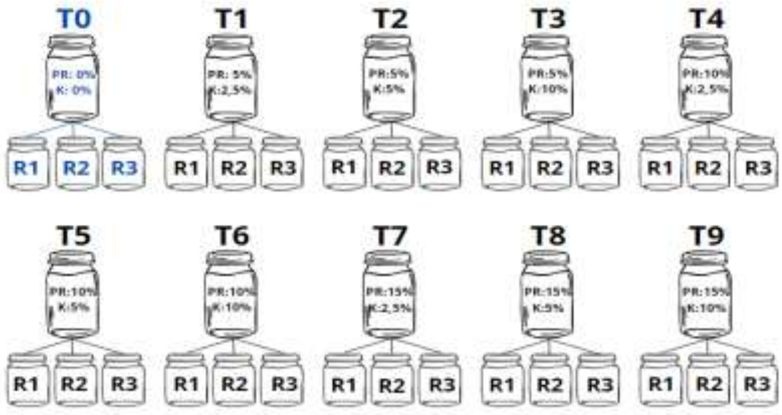

Fig. 1 Distribution of treatments in the fermentation of leachates with different P and K loads.

Analytical methods

The behavior of organic acids was determined by High-Performance Liquid Chromatography (HPLC) by using a Shimadzu LC-2030 C3D equipment located at the Animal Nutrition Laboratory of the Juan de Castellanos University Foundation in Soracá, Boyacá, Colombia. A VDSpher OptiAqua PUR 100 C18 column with a particle size of 5 µm was used and the mobile phase consisted of a water:methanol ratio of 95:5. Measurements were taken at a wavelength of 210 nm.

The monitoring of TP and W-SP was carried out using the colorimetric method of vanadomolybdophosphoric acid with a UV-Visible spectrophotometer at 420 nm, following the methodology described in the AOAC (Association of Official Agricultural Chemists).

The behavior of K was determined by using the methodology reported by Hanway & Heidel (1952). pH and EC were measured with a pH meter from Hanna and a conductivity meter. The nitrogen content was determined by using the Kjeldahl method (TKN) and the Total Organic Carbon (TOC) was analyzed by using a Multi N/C 2100 Analytik Jena analyzer located at the Catalysis group at the Universidad Pedagógicay Tecnológica de Colombia. The behavior of minerals (Na, Fe, Zn, Mg, Mn and Ca) was analyzed using an atomic absorption spectrophotometer PerkinElmer model 400, after performing a closed acid wet digestion in a Digestor™ 2508 from FOSS using sulfuric and nitric acid. Digestion was completed until the sample no longer presented any color.

Statistical analysis

The data was tabulated and analyzed by using the statistical analysis software RStudio, where tests for variance homogeneity were conducted for each variable. Analysis of variance (ANOVA) was used and Tukey's post hoc test for significant differences ($P < 0.05$) was performed to determine the differences between treatments and the correlation of the studied variables. Furthermore, Principal Component Analysis (PCA) was employed using the library "factoextra", where the correlation of the studied variables in relation to pH, P and organic acids content was observed.

Results and discussion

pH behavior

The pH results during the fermentation process are shown in Fig. 2 and standard deviations (SD) in Appendix, Table 2. The initial pH value of the leachate originating from organic matter composting was approximately 4.4, similar to the data obtained by Ebrahimi et al. (2018), García et al. (2021) and Siciliano et al. (2019, 2021), with values ranging between 3.5 and 5.5. Results showed a slight increase in pH at T0 as the fermentation progresses, rising from 3.57 on day 5 to 3.95 on day 15. This could be attributed to a reduced presence of acidic substances, as a result of microbial consortia activity (Tran et al. 2015), which can utilize easily degradable materials along with short-chain acids. In all treatments where PR concentration was kept constant and the content of K sulfate was increased, a small pH decrease was observed on day 15.

The decrease in pH in the treatments compared to the initial pH could be attributed to several causes, including the synthesis of acidic species like short-chain organic acids, which are produced through microbial-driven oxidation reactions of organic matter (Wei et al. 2016; Saeid et al. 2018). The acids responsible for the pH decrease and the action of species like sulfate which transform into sulfuric acid are discussed in the "behavior of organic acids" section below. Additionally, the data shows that the presence of PR and K contributes to the generation of acidic species and increased microbial growth (Bakhshandeh et al. 2017; Schouben et al. 2014), thus leading to slight decreases in pH over the fermentation period.

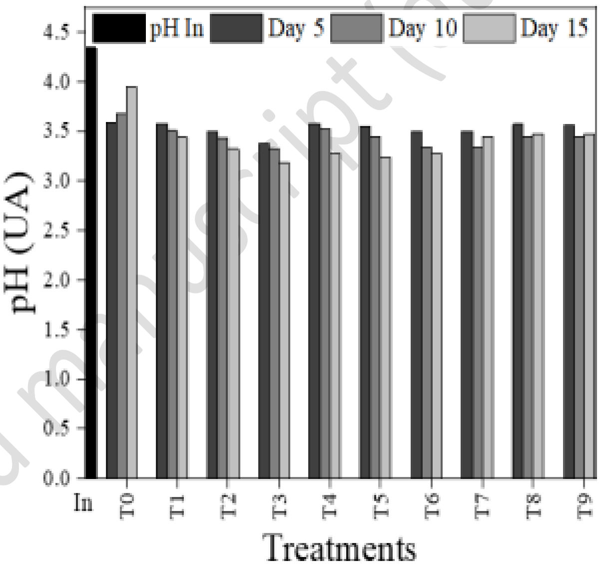

Fig. 2 pH behavior at different PR and K concentrations in fermentation process the leachate

EC behavior

The behavior of EC is shown in Fig. 3 and SD in Appendix, Table 2. The values in the fresh leachates UOSW range from 1.2 mS/cm to 34 mS/cm according to data from (Baccot et al. 2017; Ebrahimi et al. 2018; García et al. 2021; Malick et al. 2019; Roy et al. 2019; Siciliano et al. 2019, 2021), a behavior related to the source where they are generated. For instance, the initial EC of the leachate from Paipa was 17.6 mS/cm, which falls within the range found by several authors. However, it is higher than that reported by Malick et al. (2019), who found an EC of 13.6 mS/cm for leachates from the composting of fruit and vegetable waste mixed with hay or wood residues and lower than what was reported by Ebrahimi et al.

(2018) at 33.4 mS/cm. A higher presence of weak and strong electrolytes such as organic acids, dissolved minerals and chlorine (not measured) could be related to the variability in EC. For instance, reactions between calcium and sulfate might occur, since adding less PR results in more availability of K (See Fig. 5). Treatments when PR and K were added showed an increase in EC values due to a greater quantity of soluble species like P and K ions, which notably contribute to EC.

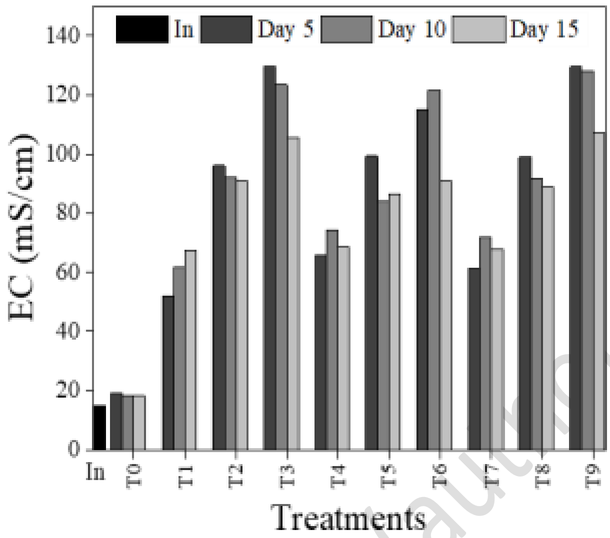

Fig. 3 EC behavior at different PR and K concentrations in the leachate fermentation process

Behavior of various forms of phosphorus

TP Behavior

The analysis of TP in the leachate under initial conditions and different treatments is shown in Fig. 4 and SD in Appendix, Table 2. The initial TP value for the Paipa leachate was 0.55 g/L, similar to the value reported by Siciliano et al. (2021) but higher than the 0.28 g/L found by Ebrahimi et al. (2018). The variability in the data is a consequence of the chemical and microbiological composition of the waste entering the composting plants, climatic conditions, storage and organic and inorganic contaminants (Cardoso et al. 2019). TP content increased gradually in the following order: treatments with 15% PR (T7, T8 and T9) > treatments with 10% PR (T4, T5 and T6) > treatments with 5% PR (T1, T2 and T3), as a result of higher PR content. These results are in line with behavior observed in other studies by evaluating different PR concentrations for the production of solid organic fertilizers (Bangar et al. 1985; Ditta et al. 2018; Lu et al. 2014; Montoya et al. 2020; Paez et al. 2022; Zhan et al. 2021). Additionally, high TP contents in the different treatments could be associated with the acidic pH and high organic matter content (microbial food), which can influence the reactivity of PR, thus increasing its solubilization and the concentration of free phosphates (Azaña et al. 2021). Finally, T0 showed a lower concentration throughout the process, compared to the initial TP content. This could be linked to microorganisms using P for their metabolic processes (Bakhshandeh et al. 2017; Schouben et al. 2014).

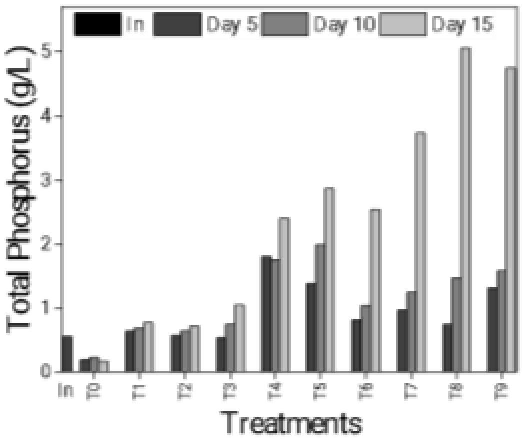

Fig. 4 TP behavior at different RP and K concentrations in the leachate fermentation process

W-SP Behavior

The results of W-SP behavior are shown in Fig. 5 and SD in Appendix, Table 2. The data revealed that approximately 69% of the initial TP of the leachate corresponds to SP. Generally, the characterization of these liquids only considers TP and there are not many data points to compare with those obtained in this study. However, we believe that the content of SP could be associated with solid-liquid mass transfer phenomena that are common during composting. Elements like P transfer to the liquid phase as plant or animal organic matter degrades through hydrolytic reactions (De Guardia et al. 2002; Krogmann and Woyczechowski 2000). Phospholipids, nucleic acids and phytates are major sources of P in this context (Corrales et al. 2014).

The data shows that treatments enriched with PR presented a higher concentration of SP compared to T0. However, when the PR concentration increased from 10% to 15%, there was a decrease in SP of approximately 13%. Additionally, concentrations of 5% and 10% PR showed a similar behavior in SP content. This phenomenon has been reported in studies of organic matter stabilization through composting, where increasing PR levels decrease the amount of W-SP. The former has been linked to reactions of P with other species, such as CaO present in PR and minerals added at the beginning of the process (Kutu et al. 2019; Paez et al. 2022; Singh 2012). In this study, the behavior is favored by all components being in a liquid medium, thus allowing for greater substance mobility, increasing the likelihood of effective collisions and generating interactions and chemical reactions. Furthermore, the data indicates a higher amount of SP in the treatments with 5% and 10% PR, which could be associated with a greater presence of substances like short-chain organic acids such as formic, citric, oxalic, lactic, acetic, butyric acids, among others, which allow the P present in PR to become soluble forms through chelation processes involving their hydroxyl and carboxyl groups (Bustamante et al. 2016; Saeid et al. 2018). The presence of these acids could be linked to the activity of various microorganisms like *Bacillus, Arthrobacter, Penicillium, Aspergillus, Micrococcus and Streptomyces* (Banik and Dey 1982; Escobar and Solarte 2015). The presence of certain acids like lactic, acetic, propionic, citric and tartaric was confirmed in this study and will be discussed in the "behavior of organic acids" section below. Finally, the data reveals that the increase in K content has a positive effect on SP concentration in all treatments, thus being more pronounced in treatments with lower

PR content (5% and 10%). On the other hand, authors like Nath et al. (2017) suggest that K plays a role like that of P, thus being necessary for the biological processes of microorganisms.

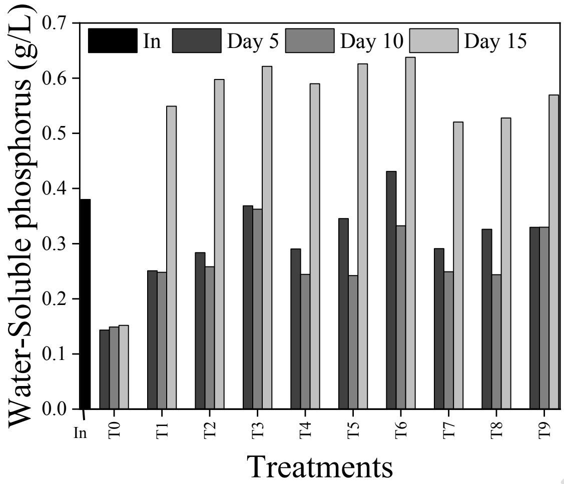

Fig. 5 W-SP behavior at different PR and K in fermentation process the leachate

K behavior

The results exhibit a typical behavior of K (Fig. 6) and SD in Appendix, Table 2, where the highest concentrations are observed in treatments with a higher content of K_2SO_4. Additionally, the initial concentration of K (originating from household waste) is around 600 ppm, similar to the value reported by Siciliano et al. (2019) who found 500 ppm in compost leachates. The K content in T0 remained relatively unchanged throughout the process, which could be attributed to a lower presence of microorganisms promoting the decomposition of organic matter, then leading to less K solubilization (Ahmad et al. 2016). On the other hand, the gradual increase in K during fermentation (5, 10 and 15 days) might be linked to the presence of microbial consortia, such as phosphorus solubilizers which have been shown to impact K solubilization through the action of organic acids, increasing both K and P concentrations (Bakhshandeh et al. 2017; Adeleke et al. 2017).

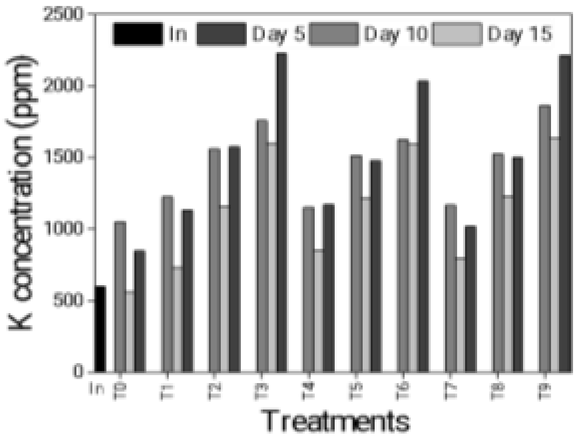

Fig. 6 Potassium behavior at different PR and K concentrations in fermentation process the leachate

Organic acids behavior

The behavior of organic acids on days 5, 10 and 15 was determined using HPLC based on the equations derived from the calibration curves of each standard (Appendix, Table 3). The analysis of the samples (Fig. 7) showed the presence of five predominant short-chain organic acids: AA, LA, CA, PA and TA. The results indicate that the highest concentrations of LA were found on days 5 and 10 in the range of 15,000 to 20,000 ppm. However, on day 15, the content decreased in all treatments by 85% to 90%, except for T0 where LA was not detected. A similar pattern was observed for CA, with concentrations between 14,000 ppm and 17,000 ppm on days 5 and 10, decreasing by 65% to 75% on day 15 in each treatment. Additionally, the SD can be seen in Appendix, Table 2.

The content of AA on day 5 ranged from 6,900 ppm to 7,400 ppm for treatments with PR and K_2SO_4. By day 10, there were increases of 35% and 43%, respectively. Furthermore, on day 15, there were increases of 175% and 205%, respectively, resulting in AA concentrations ranging from 21,000 ppm to 31,000 ppm. Finally, the PA content decreased by 8% to 10% from day 5 to day 10. However, on day 15, there were increases of 145% to 182%, with concentrations ranging from 26,000 ppm to 35,000 ppm for the different treatments.

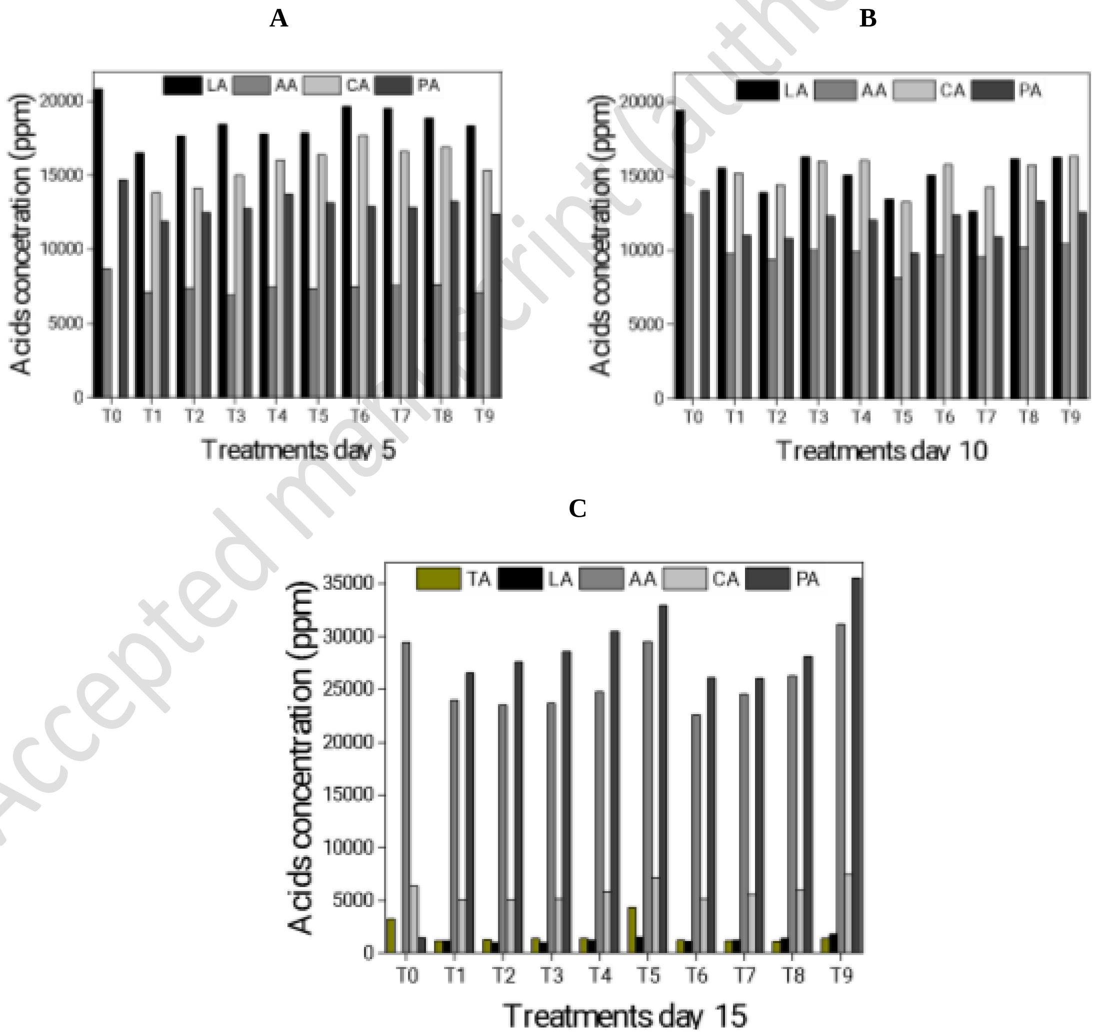

Fig. 7 Behavior of organic acids in the fermentation of leachate with different K and P concentrations

The content of these organic acids may be associated with the decomposition of organic matter such as carbohydrates, peptides and lipids, as well as microbial fermentation by certain bacteria and fungi (Adeleke et al. 2017; Onireti et al. 2017). LA in the leachate might be linked to the presence of lactic acid bacteria, primarily of the genus *Lactobacillus,* which can ferment simple biomolecules (monosaccharides and disaccharides) in the leachate storage tank, as well as during the dehydration stage of UOSW, transferring LA to the liquid phase. In these two stages of the process, oxygen levels can decrease, thus favoring anaerobic processes. The presence of *Lactobacillus* genus microorganisms in leachates from MSW was reported by Yadav et al. (2014), who found species like *Lactobacillus acidophilus, Lactobacillus casei* and *Lactobacillus fermentum.* Higher concentrations of LA were observed in the early fermentation days and remained until day 10. Finally, we believe that LA was consumed by microbial consortia as a food source, leading to the decrease in concentration on day 15.

The content of AA may be related to the presence of acetic acid bacteria known as *Acetobacter sp.* These are gram-negative aerobic bacteria which can be found in the class *Alphaproteobacteria,* order *Rhodospirillales* and family *Acetobacteraceae* (Kersters et al. 2006). They were identified in leachates from a composting plant in Mexico, where *Proteobacteria* was determined as the third predominant phylum (Bravo et al. 2019). The main metabolic pathways of these bacteria for AA production include the respiratory chain oxidizing alcohol, the Krebs cycle, the pyruvate metabolic pathway and the pentose phosphate pathway. The incomplete oxidation of simple monosaccharides is the most significant process in AA formation (Li et al. 2015; Sengun 2017). Additionally, studies by Beltrán (2014) reported that some strains of *Bacillus liqueniformis* and *B. amyloliquefaciens* produce mixtures of LA and AA. On the other hand, Tran et al. (2015) observed that the production of LA in high concentrations can inhibit the production of AA; with results comparable to those obtained during the preparation of LOFM. For instance, it was observed that the concentration of LA was between 13,000 ppm and 19,000 ppm on days 10 and 15, whereas the concentration of AA remained between 7,000 ppm and 10,000 ppm. However, when the concentration of LA decreased within the range of 1,000 ppm and 3,000 ppm of LA, the content of AA increased significantly on day 15 (Fig. 6).

The production of CA was the highest between days 5 and 10 and could have been influenced by the presence of fungi of the *Aspergillus genus* (Papagianni 2007), which use monosaccharides and disaccharides (mainly sucrose) as carbon sources for CA production (Ghazala et al. 2019). Additionally, Papagianni (2004) and Velásquez et al. (2010) indicated that CA production is proportional to the consumption of sugars by microorganisms. This behavior could explain the low levels of CA concentration obtained in T0 where molasses was not incorporated. Papagianni (2007) also notes that the presence of CA is favored when high concentrations of sugars (weed incorporation) and an acidic environment (generation of acidic species) are present. Finally, the results show a decrease in CA on day 15, possibly because of reduced sugar content or because it was utilized as an energy source by microbial consortia.

During the study, an increase in PA content over time was observed (Fig. 6), with the highest concentrations occurring on day 15. These results could be linked to low oxygen levels resulting from increased microorganism presence due to the high availability of nutrients (molasses), macro and micronutrients and the intermittent agitation system which did not allow for homogeneous oxygenation. This behavior was evident only in the treatments where the P, K and molasses source were added; for T0, the PA content was much lower than that of the other treatments. The presence of PA could have been generated through fermentative, biosynthetic and catabolic pathways of amino acids (Parvathy et al. 2019; Tufvesson et al. 2013). Finally, the presence of TA on day 15 could be related to the potential growth of bacteria like *Acinetobacter tartaricus* or *Pseudomonas agrobacterium*, which have demonstrated enzymatic activity in producing this acid. For instance, Goldberg and Stefan Rokem (2019) identified *Acinetobacter* in leachates from a composting plant.

Macronutrients and micronutrients in LOFM

The behavior of minerals on day 15 is shown in Table 1. The presence of minerals in leachates is a consequence of organic matter degradation processes and the quantity is dependent on the nature of the source producing the leachate and degradation conditions (Chatterjee et al. 2013). Thus, Malick et al. (2019) summarized concentration ranges for Mg (59-153 mg/L), Ca (70-614 mg/L), K (359-9000 mg/L), Na (46-1044 mg/L) and Zn (0.5–43900 mg/L); only the Ca found in this study falls outside these ranges. The positive and significant regression coefficients for PR 10% and PR 15% in the TOC content, with values of 8.90 and 11.45, respectively, indicate an increase in TOC with the increase in the concentration of PR (Apendix 4). However, the values of TKN were within the range (0.01-0.8 g/L) found by the same author. Additionally, an increase in TOC and organic N was observed in treatments with the addition of PR and K sulfate, attributed to the increments of inorganic C and N from the urea added to the fermentation process. The content of Fe and Ca increased with the increase in PR and K content, with the lowest values in the control treatment and the highest in treatments T7, T8 and T9. The increase in Ca aligns with the increase in PR due to the contribution of CaO. However, the higher Fe values in the final treatments could be related to the presence of acids that favored the solubility of iron sulfate. Otherwise, Zn, Mg and Mn showed a similar behavior in all treatments, thus indicating that these minerals are not drastically affected by system conditions such as pH, the presence of acids and P and K species. The regression coefficients for PR 10% and PR 15% show a significant decrease in sodium concentration (-28.14 and -30.06), respectively. These results suggest that as the concentration of PR increases, the sodium concentration tends to decrease (Apendix 4). Besides, the content of Na was lower in treatments where a P and K source was added compared to T0. The decrease of approximately 63% (averaged value) could be related to the assimilation of this mineral by microorganisms to fulfill metabolic processes, as reported in previous studies (Paez et al. 2022), without ruling out interactions between Na and other chemical species such as H2PO4 from PR and sulfates derived from the mineral source.

Thus, the potential effects of an organic fertilizer rich in organic acids can aid in the availability and absorption of nutrients which may be deficient, unavailable, or insoluble in the soil. This can promote plant growth and enhance food production, while also reducing the reliance on commercial fertilizers, which have shown detrimental effects on soil health. Fertilizers produced through fermentation, like this one, represent a strategy to improve soil health due to their nutrient content and microbial components.

Table 1. Behavior of micro and macronutrients in the fermentation of Paipa leachates on day 15

Mineral	Unit	L_{In}	T0	T1	T2	T3	T4	T5	T6	T7	T8	T9
Zn		9.10	1.61±1.01	70.59±5.21	68.97±2.00	67.42±5.74	69.65±10.38	59.64±7.11	57.37±0.68	60.75±3.09	57.40±3.95	66.23±2.99
Mg		76.15	65.54±4.85	196.18±17.64	208.57±12.15	205.86±10.55	215.02±18.50	196.13±13.69	186.31±3.29	19.11±4.96	188.55±11.73	204.42±3.79
Na	**ppm**	100.12	84.00±10.24	56.92±27.03	27.94±1.61	31.18±2.45	28.78±2.62	27.80±3.21	33.04±3.58	26.85±0.48	30.71±2.36	33.00±9.65
Fe		2.02	13.96±2.24	67.36±4.87	71.64±11.94	72.04±2.55	82.56±13.07	76.94±19.43	77.77±14.65	89.33±1.45	99.87±2.97	107.09±6.56
Mn		13.53	0.00±0.00	20.55±0.15	20.10±0.26	20.30±0.18	18.80±0.74	18.71±0.67	18.37±0.23	18.16±0.69	18.24±1.74	16.99±2.17
Ca		990.56	1011.16±182.93	2728.56±2225.82	2280.22±275.67	2965.32±233.60	2731.18±342.82	2754.50±258.92	2605.90±215.63	3492.53±453.57	3979.07±646.03	4737.98±50.42
TOC		35.13	30.12±1.64	39.09±7.32	42.77±1.48	45.88±1.63	47.99±1.38	48.35±0.66	49.655±0.56	50.56±1.78	49.56±1.08	47.76±1.05
TKN	**g/L**	0.33	0.65±0.06	5.53±0.03	5.39±0.07	5.58±0.06	5.03±0.53	5.42±0.06	5.229±0.12	5.56±0.10	5.22±0.01	5.09±0.26
C/N	**g/L**	106.45	46.27±7.08	7.06±1.36	7.94±0.38	8.23±0.20	9.54±1.30	8.92±0.22	9.50±0.12	9.08±0.14	9.50±0.18	9.38±0.27

Mean±standard deviation. See regression coefficients in Appendix, Table 4.

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Statistical analysis

In the Fig. 8, the Pearson correlation data is displayed. The data shows a strong positive correlation between total P and LA, AA and CA and LA and PA ($0.7 < r < 1$). This could be associated with the fact that the release of P from PR is influenced by the presence of organic acids, which have the potential to enhance P mobility by reducing the pH of the medium (Adeleke et al. 2017). TP is primarily influenced by LA, AA and CA, which are key mediators in the process of P solubilization (Adeleke et al. 2017; Patiño-Torres and Sanclemente-Reyes 2014). pH negative correlates with SP due to the interaction involved in the solubilization of P present in PR through its hydroxyl and carboxyl groups (Paez et al. 2022). Additionally, K shows a moderate positive correlation with the variable PA. Similarly, a moderate positive correlation exists between TA and CA, as well as AA ($0.5 < r < 0.7$). On the other hand, pH exhibits a strong negative correlation with SP ($r=-0.39$) and a moderate negative correlation with TA and K ($r=-0.42$ and $r=-0.31$), respectively.

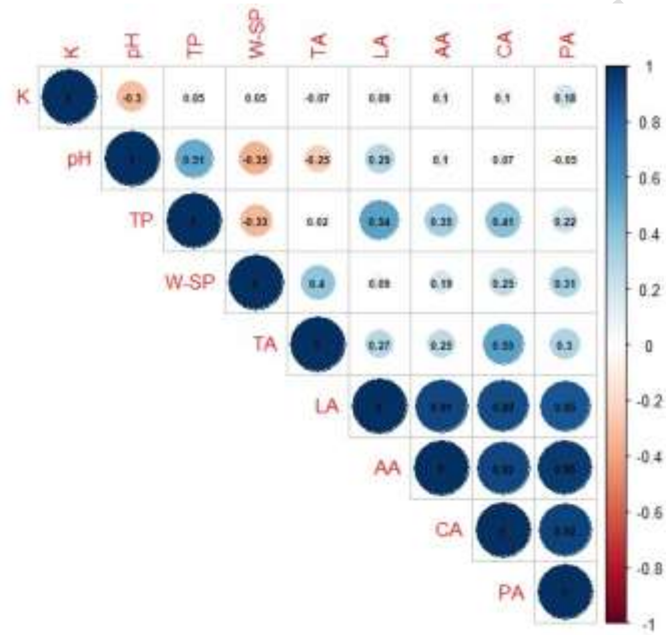

Fig. 8 Pearson Correlation for the variables K, pH, TP, W-SP, TA, LA, AA, CA and PA in the fermentation process of the leachate.

In Fig. 9, PCA is presented, showing that the first two principal components accounted for 69.7% of the total variability. In component 1, the variables with the highest contributions are LA, AA, CA and PA (21.5%, 21.8%, 23.32% and 21.10%) respectively. The Biplot demonstrates that these variables are positively associated. In component 2, the variables pH, TP and SP had the greatest contributions to this component (33.67%, 22.65% and 26.45%) respectively. Additionally, pH and TP have a positive association, whereas having a negative association with SP and TA. On the other hand, treatment 9 exhibits the highest levels of acids, while treatment 8 stands out for having the highest levels of pH and TP. Also, the treatment 3 shows the lowest values for these variables.

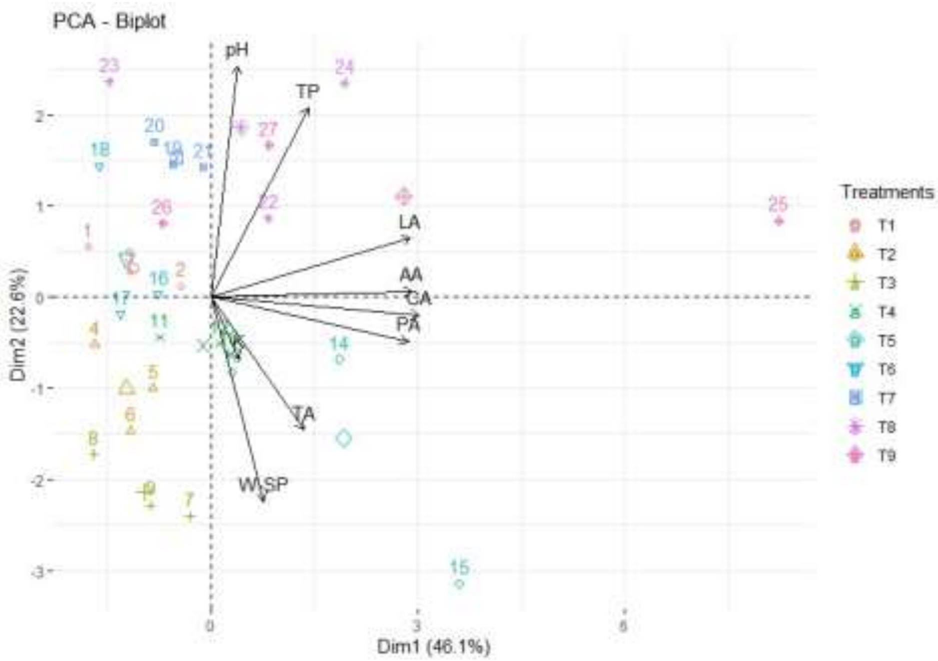

Fig. 9 Principal component analysis in fermentation process the leachate with different K and P concentrations.

Conclusion

The addition of PR as a source of P and K sulfate as a source of K to the leachate from UOSW modified the behavior of nutrients, especially the contents of K and P, but did not significantly affect the behavior of organic acids in each treatment. The incorporation of low-cost mineral sources to produce organic liquid fertilizers can be extremely beneficial for soil health, thus providing essential nutrients to plants (Na, Zn, Ca, Mn, Mg, Fe, K and P). Additionally, the use of leachate from UOSW for the production of LOFM can reduce the amount of waste going to landfills and thus minimize the environmental impact of waste disposal.

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Appendix

Table 1. Experimental matrix of the 3x3 factorial design

PR	K	TOC	KTN	C/N	Zn	Fe	Mg	Mn	Ca	Na
5	2.5	39.09±7.32	5.53±0.03	7.06±1.36	70.59±5.21	67.36±4.87	196.18±17.64	20.55±0.15	2728.56±2225.82	56.92±27.03
10	2.5	42.77±1.48	5.39±0.07	7.94±0.38	68.97±2.00	71.64±11.94	208.57±12.15	20.10±0.26	2280.22±275.67	27.94±1.61
15	2.5	45.88±1.63	5.58±0.06	8.23±0.20	67.42±5.74	72.04±2.55	205.86±10.55	20.30±0.18	2965.32±233.60	31.18±2.45
5	5	47.99±1.38	5.03±0.53	9.54±1.30	69.65±10.38	82.56±13.07	215.02±18.50	18.80±0.74	2731.18±342.82	28.78±2.62
10	5	48.35±0.66	5.42±0.06	8.92±0.22	59.64±7.11	76.94±19.43	196.13±13.69	18.71±0.67	2754.50±258.92	27.80±3.21
15	5	49.655±0.565	5.229±0.12	9.50±0.12	57.37±0.68	77.77±14.65	186.31±3.29	18.37±0.23	2605.90±215.63	33.04±3.58
5	10	50.56±1.785	5.56±0.10	9.08±0.14	60.75±3.09	89.33±1.45	197.11±4.96	18.16±0.69	3492.53±453.57	26.85±0.48
10	10	49.56±1.085	5.22±0.01	9.50±0.18	57.40±3.95	99.87±2.97	188.55±11.73	18.24±1.74	2728.56±2225.82	56.92±27.03
15	10	47.76±1.05	5.09±0.26	9.38±0.27	66.23±2.99	107.09±6.56	196.18±17.64	20.55±0.15	2280.22±275.67	27.94±1.61

Table 2. Standard deviations of the parameters measured at 5, 10 and 15 days in the fermentation of the leachate

Treatment	K	pH	EC	TP	W-SP	TA	LA	AA	CA	PA
Day 5										
T0	89.71	0.01	0.67	0.02	0.01		2451.12	3938.11	0.00	1566.27
T1	52.24	0.01	12.24	0.08	0.03		1079.35	2435.66	1191.98	1080.64
T2	163.54	0.01	14.85	0.03	0.08		2399.84	860.05	2323.18	1709.10
T3	96.76	0.04	16.20	0.02	0.06		1808.78	731.39	1510.11	1424.63
T4	82.03	0.01	7.63	0.49	0.01	0.00	488.94	216.09	184.97	651.26
T5	157.36	0.00	3.66	0.35	0.02		274.02	468.56	420.41	129.18
T6	102.98	0.02	14.09	0.06	0.01		1567.43	407.45	1600.75	888.96
T7	61.59	0.02	13.10	0.12	0.02		839.96	441.06	440.35	591.90
T8	11.60	0.01	8.96	0.01	0.02		523.69	137.90	130.02	117.07
T9	38.72	0.01	11.85	0.37	0.03		1608.49	755.68	1025.97	1358.92
Day 10										
T0	62.15	0.01	1.28	0.01	0.02		4614.88	2920.79	0.00	3362.20
T1	52.27	0.02	19.00	0.03	0.03		3275.59	1829.50	3221.27	2757.95
T2	102.42	0.01	13.88	0.08	0.03		1291.48	632.85	1025.04	1023.74
T3	120.56	0.02	8.20	0.03	0.04		1244.19	532.40	712.57	798.80
T4	56.18	0.01	8.63	0.06	0.02	0.00	719.37	221.72	192.91	310.12
T5	158.21	0.01	2.63	0.06	0.06		3885.25	1128.16	3322.38	2422.06
T6	102.87	0.01	13.71	0.09	0.05		1422.79	873.59	1555.02	891.13
T7	46.72	0.01	7.90	0.07	0.06		1636.58	654.12	1022.18	1123.54
T8	84.39	0.02	2.08	0.25	0.02		1173.76	340.36	619.09	1229.38
T9	72.59	0.03	1.93	0.33	0.03		142.39	670.49	1031.50	961.57
Day 15										
T0	90.08	0.04	0.11	0.01	0.00	169.94	0.00	985.11	577.72	241.90
T1	13.92	0.02	1.57	0.02	0.03	124.38	107.85	1642.45	356.75	2269.70
T2	63.90	0.04	1.86	0.10	0.03	50.64	219.27	866.19	313.84	1775.81
T3	95.26	0.06	4.66	0.02	0.05	71.38	264.67	1014.87	260.23	1453.99
T4	70.55	0.02	5.53	0.47	0.00	89.99	153.54	693.83	486.21	2602.31
T5	150.40	0.02	5.43	0.10	0.04	5144.55	184.09	2599.33	1659.27	2855.22
T6	83.06	0.10	3.01	0.19	0.04	76.80	58.18	1388.38	266.34	2175.67
T7	30.05	0.01	5.58	0.43	0.02	39.37	43.84	716.28	288.25	783.55
T8	110.30	0.01	5.62	1.06	0.06	193.91	263.35	5867.49	1196.22	5325.49
T9	34.83	0.01	4.23	1.07	0.02	700.86	756.26	13645.83	3168.42	15620.01

Table 3. Calibration curve equations for organic acids standard

Acid	Curve equation	R^2	Retention time (min)
Tartaric	y = 2956.4x -2632	0.999	8.9
Lactic	y = 2332.6x - 813.87	0.999	10.4
Acetic	y = 1414.4x - 255.33	1.000	11.8
Citric	y = 2274x + 353.53	0.999	13.8
Propionic	y = 1234.5x – 177	1.000	16.9

Table 4. Regression coefficients of micro and macronutrients in the fermentation of Paipa leachates on day 15

Coefficients	TOC	KTN	C/N	Zn	Fe	Mg	Mn	Ca	Na
PR 10%	8.90**	-0.50**	2.56***	-0.93	15.20.	18.84***	-1.74.	2.68	-28.14**
PR 15%	11.45**	0.03	2.01**	-9.83*	21.97*	0.93.	-2.38*	763.96*	-30.06**
K 5%	3.68	-0.14	0.87	-1.62	4.28	12.39	-0.44	-448.34	-28.98**
K 10%	6.79*	0.04	1.15*	-3.16	4.68	9.68	-0.25	236.75	-25.74**
PR 10%:K 5%	-3.32	0.53	-1.15.	-8.38	-9.90	-31.29*	0.35	471.66	28.00*
PR 15%:K 5%	-4.68	-0.19	-0.46	-1.72	6.26	-20.96	0.52	934.88*	32.83**
PR 10%:K 10%	-5.13	0.15	-1.29	-9.12	-9.48	-38.39*	-0.17	-362.03	30.00*
PR 15%:K 10%	-9.59**	-0.5145*	-0.85	8.64	13.08	-2.36	-0.91	1008.69*	31.89*

Significance p< 0 '***' p< 0.001 '**' p<0.01 '*' p< 0.05 '.'