



## Alternative amendment for vineyards from by-products of pyro-bituminous shale: Effect on wine amino acids and biogenic amines



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### ABSTRACT

With the aim of looking for a model of agroecological production, the use of by-products from pyro-bituminous shale as amendment, and its effect on wine amino acids and biogenic amines has been evaluated. Field trials aimed to compare the effect of different doses of conventional and limestone shale from by-products of pyro-bituminous. Four replicates for six different fertilization treatments were arranged in a split plot design during 2009/2010 and 2010/2011 vintage. A chromatographic analysis was carried out to evaluate the impact of fertilization treatments on the amino acid and biogenic amine content of wines produced. Results showed few significant differences among fertilization treatments tested according to the amino acids composition of wines, although it seemed that a combination of conventional and pyro-bituminous shale could be the best option. By-products of pyro-bituminous shale seem to be a good partial substitutive amendment for Brazilian vineyards. This research seems to be a new approach for sustainable revalorization of domestic fertilizers to enable minor environmental impacts and lower production costs without detriment to quality.

### 1. Introduction

The effect of different viticultural practices in grape and wine composition has been evaluated by many authors. Several practices as irrigation, fertilization, and cover crop practice influence the regulation of nutrient and water availability of vines and can indirectly affect grape and wine composition (Gil et al., 2013; Jackson & Lombard, 1993).

Soil fertilization and amendment is one of the most common viticultural techniques used, due to its beneficial effect on vineyard performance. However, excessive or unbalanced application can imply undesirable effects on grape quality (Delgado, Martín, del Álamo, & González, 2004). Nitrogen fertilization has been reported to have a substantial impact on grape and wine composition, including phenolic compounds and amino acids (Bell & Henschke, 2005; Garder-Cerdán et al., 2014; Smit et al., 2014).

Different types of organic amendments applied to a Cabernet Franc vine, produced lower color intensity and more aromatic persistency in wines (Morlat & Symoneaux, 2008). Application of winery and distillery waste composts to a vineyard caused an increase of available soil macro and micronutrient contents and a slow release of inorganic N

(Bustamante, Said-Pullicino, Andreu, Paredes, & Moral, 2011).

In recent times, the use of biochar, a carbon-rich material made by heating organic matter at high temperature, as soil amendment has been investigated. Biochar produces many benefits to soil, increasing the cation exchange capacity and the sorption of organic matter (Liu, Feng, & Zhang, 2012).

Brazilian soils are characterized by high acidity and aluminum and manganese toxicity as well as deficiencies in calcium, magnesium and phosphorus which affect the root development and plant productivity (Silva, 2012). To overcome this limitation, the liming soil technique is often employed, which involves the application of basic formulation such as calcium and magnesium rich materials to soils with the aim to neutralize acidity and improve the chemical and physical soil characteristics (Bernier & Alfaro, 2006).

Brazil is one of the most importers of fertilizers and amendments. This fact results in a heavy reliance on other countries and risks of instability as well as higher production costs to meet internal demand. Therefore, researching into the development of alternative fertilizers or amendments based on by-product revalorization from domestic industries is fundamental for the progress of Brazil as viticulture country. Exploit natural resources not only results in important economic

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benefits but also in the development of more sustainable agroecological production.

The pyro-bituminous oleifera shale rock is composed by a large amount of hydrocarbons disseminated in a mineral medium known as kerogen, whose thermal decomposition produces oil and other co-products (Fonseca, Nascimento, Santos, & Neto, 1989). Consequently, Brazil is one of the leading global producers of shale-derived products (such as fuel oil, gas, naphtha, and sulfur). Among them, the limestone shale has been postulated as a by-product of great agronomic importance due to its macro and micronutrient content essential for plant development (Malagi, 2011). In addition, the occurrence of calcium and magnesium oxides in limestone shale could be useful to neutralize the acidity of Brazilian soils.

In the recent years, the effects of by-products of pyro-bituminous shale in agronomic production of different products have been evaluated. The use of the shale as amendments in vineyards affects wine phenolic composition positively (Alañón et al., 2016), while foliar fertilization with shale products resulted in an increased crop production of corn, lettuce and tomato and resulted also in an improvement of their qualities (Messias, 2011; Pereira & Melo, 2002). However, the effect of vineyards fertilization with pyro-bituminous shale on the nitrogenous compounds in wines resulted has not been evaluated yet.

Therefore, with an eye towards the total or partial substitution of conventional limestone by shale limestone as sustainable domestic amendment, a field trial was conducted during two consecutive vintages to assess the effect of different amendment treatments on the amino acid and biogenic amine content of wine produced.

## 2. Materials and methods

### 2.1. Vineyards and amendment experience

Cabernet Sauvignon (*Vitis vinifera* L.) vineyard of eight years old, grafted on rootstock Paulsen 1113 (*Vitisberlandieri* × *Vitisrupestris*), was placed in the experimental station of EPAGRI (Empresa de Pesquisa e Extensão Agropecuária de Santa Catarina), in Videira, SC, Brazil, under coordinates 27° 02' 04" south latitude and 51° 08' 05" longitude west. A "Latada" (Trellised Vine) system of conduction was employed.

The climate, according to Köppen-Geiger classification, was classified as CFA: mesothermal climate-warm temperature climate. Average temperatures were 16–18 °C, and the average annual rainfall was around 1800 mm and the soil was classified as RhodicPaleudult. Detailed climatic data during the production cycle of the grapevines in 2009/2010 and 2010/2011 harvests are shown in Fig. 1.

Chemical composition of shale limestone (SL) and conventional limestone (CL) was provided by X-ray fluorescence (Table 1). Shale limestone was rich in SiO<sub>2</sub>, CaO, MgO and Al<sub>2</sub>O<sub>3</sub> content joint high percentages of FeO<sub>3</sub>, K<sub>2</sub>O and Na<sub>2</sub>O. The potential of shale limestone (SL) alone or in combination of conventional limestone (CL) to be used as fertilizer was evaluated by means of an experimental design carried out in randomized blocks. Four replicates for six different amendment treatments (Table 2) were arranged in a split plot design. A total of 24 plots with 15 vines each were under study for data collection. The amendment process was established taking into account the recommendation of liming based on previous analysis of soils from vineyard. The cover crop mixtures of the two amendments were conducted on the first half of July 2009 on vines from Cabernet Sauvignon variety. The application of the amendment treatments was done one-time, manually, without extra soil and covering a meter on each side of the rows of plants. The study was carried out during 2009/2010 and 2010/2011 vintage.

At harvesting, the cluster number and the mean cluster weight was monitored for randomly chosen 15 vines in both vintages. The grape production and pruning weight were calculated in response to each amendment treatments. Ravaz index, which is the most commonly used crop load calculation, was also determined as yield from the harvest

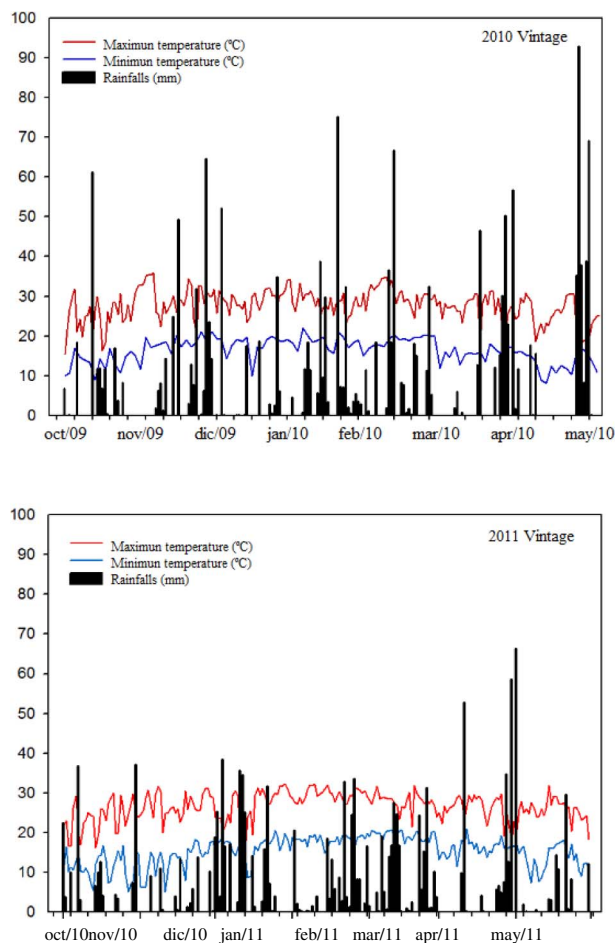


Fig. 1. Maximum and minimum temperatures (°C) and rainfalls (mm) during the production cycle of the grapevines for 2010 and 2011 harvests.

Table 1

Chemical composition expressed in percentage of shale and conventional limestone products measured by X-ray fluorescence.

Composition (%)	Shale limestone	Conventional limestone
SiO <sub>2</sub>	47.46	14.78
CaO	16.0	28.8
MgO	14.9	18.5
Al <sub>2</sub> O <sub>3</sub>	9.25	0.91
FeO <sub>3</sub>	5.29	0.52
K <sub>2</sub> O	1.76	0.32
Na <sub>2</sub> O	1.26	0.22
TiO <sub>2</sub>	0.41	0.03
P <sub>2</sub> O <sub>5</sub>	0.23	0.04
MnO	0.13	0.03
Cr <sub>2</sub> O <sub>3</sub>	0.007	< 0.002
C	9.14	8.88
S	2.75	0.05
Loss on ignition	21.4	35.5

against the pruning weight. The pulp of 300 g of berries randomly selected from different plots was pressed and the juice was analyzed for total soluble solids (°Brix), pH and titratable acidity according to ECC 2676 standard procedure (1990) (Table 3).

### 2.2. Winemaking

Grapes from *Vitis vinifera* var. Cabernet Sauvignon were harvested at the optimal maturity stage during 2009/2010 and 2010/2011 vintages. Grapes were destemmed and crushed. The pomace was mixed with

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