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Research Papers

Activity of Italian natural chabasite-rich zeolitites against grey mould, sour rot and grapevine moth, and effects on grape and wine composition

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Summary. The activity of Italian chabasite-rich zeolitites for control of grey mould, sour rot and grapevine moth was compared to that from synthetic fungicides and insecticides in three vineyards in the Abruzzo region of Italy. Persistence of zeolitites on grapevine canopies has enabled applications to be carried out before rainfall events, which are likely to predispose for infections by grey mould and sour rot pathogens. Applications for control of *Lobesia botrana* (grapevine moth) were carried out after the peak of the male flight, and the presence of eggs on grape berries was also assessed. Disease and pest control were very satisfactory and comparable to those obtained from synthetic fungicides and insecticides. In addition, there were no differences among treatments for yield, berry composition, or wine ethyl alcohol, pH and total acidity. Phenolic compounds increased in wine from zeolitite-treated plants where the treatment was carried out within 15 days from grape harvest. These promising results have strategic value, because zeolitites provided simultaneous control of grey mould, sour rot and *L. botrana*. However, since these compounds have been tested for the first time for the control of diseases and *L. botrana*, the results obtained in this study require further validation.

Keywords. Zeolites, vineyard, *Botrytis cinerea*, *Lobesia botrana*.

INTRODUCTION

Botrytis cinerea (= *Botryotinia fuckeliana;* Johnston *et al.*, 2014) and *Lobesia botrana* (Denis and Schiffermüller) (Lepidoptera: Tortricidae) are among the major diseases and pests of grapevine worldwide.

Control of grey mould, caused by *B. cinerea*, is not always effective, despite the use of specific fungicides, and incurs severe economic effects for grape production (Gullino, 1992; Elad *et al*., 2007). During growing seasons characterized by rainy and wet conditions, up to 40–60% reduction in grape yields can be result from grey mould epidemics, leading to deterioration of organolectic characteristics of must and wine (Pearson and Goheen, 1988; Dubos, 2000; Elad *et al*., 2007). This pathogen is widespread in all vine-growing areas and is particularly aggressive against grapevine cultivars with tight bunches (Marois *et al*., 1986).

The pathogenic activity of *B. cinerea* is due to the ability of the fungus to synthesize lytic enzymes such as laccase and polygalacturonase (Nakajima and Akutsu, 2014), and secondary metabolites such as oxalic acid, which in turn increase the activity of polygalatturonases and laccases (Manteau *et al*., 2003), and botrydial, a phytotoxin which causes necrosis of plant cells (Colmenares *et al*., 2002).

Control of *B. cinerea* is based on at least two fungicide applications each growing season, the most important carried out at the pre-bunch closure growth stage, particularly for compact cluster cultivars. This is to protect micro-wounds that are very susceptible to the pathogen, and to reduce inoculum sources. The second application is usually during ripening, based on prevailing environmental conditions (Marois *et al*., 1986).

Leaf removal at the end of flowering improves the effectiveness of the fungicide applications. The removal of the leaves may also lead to greater coverage uniformity of the fungicide on berries and provide drying conditions that reduce bunch rot development (English *et al*., 1993; R'Houma *et al*., 1998). Removal of leaves at the 'pea-size berries' stage can also reduce infestations of *L. botrana* (grapevine moth), which in turn may favour *B. cinerea* infections from the insect feeding wounds produced on bunches (Pavan *et al*., 2016).

Effective *B. cinerea* control strategies are also based on the control of other biotic agents which facilitate occurrence of the pathogen (powdery mildew, grapevine moth), and on the correct adoption of cultural practices aimed at a reducing humidity inside grape bunches.

The use of anti-*Botrytis* fungicides can also cause residues in the harvested grapes, with different negative effects for end users, and possible onset of resistant pathogen strains (Fillinger and Elad, 2016).

In Italian vineyards, *L. botrana* has three generations per year (Pavan *et al*., 2006). After emergence, the females lay eggs on flower buttons, which can be slightly damaged by the first-generation of larvae hatched from eggs. Serious damage is caused by the second and third generations of larvae that penetrate and hollow out the berries, making the bunches more susceptible to grey mould, sour rot, and powdery mildew.

Treatments against *L. botrana* are carried out based on thresholds assessed as the presence of eggs or holes on berries in vineyards normally infested by the moth, or as 5% of bunches infested by the second and third generations in vineyards normally not infested after monitoring of the male flight activity.

Restrictions on the use of synthetic products are increasing in all wine-growing areas, for environmental protection and to limit the onset of resistant pathogen and pest strains. Application of natural compounds for management of grey mould and grapevine moth would contribute to improved production health and safety and reduce potential environmental impacts of pesticides.

Zeolites are tectosilicates and consist of a mineral family with 52 mineral species (Passaglia and Sheppard, 2001; Jha and Singh, 2016). Natural zeolites have alumino-silicate frameworks whose structures contain cavities and channels filled with water and exchangeable cations. The compensating cations may move out from the crystal structures and be replaced by other cations possessing the same positive charge (Cation Exchange Capacity; CEC). In addition, water in the channels may be removed heating from 25 to 250°C. After cooling to room temperature, water can be naturally restored (reversible dehydration). Bish and Ming (2001) and Eroglu (2014) have summarized information on zeolite crystal structure, composition, occurrence, properties and applications. For each application pure zeolites are not employed, but zeolite-rich rocks ("zeolitites") are used, and these have high contents (> 50%) of pure zeolite. The most common zeolite species in zeolitic rocks are clinoptilolite, common in many parts of Europe, and chabasite and phillipsite, which are common in different regions of Italy (Eroglu, 2014).

The effectiveness of zeolitic rocks for practical applications depends both on zeolite type and concentration. Italian chabasite-rich zeolitites are well known for their high performance for several applications (Passaglia and Sheppard, 2001). The agricultural potential of zeolites, due to their CEC (ranging from 100 to 300 meq/100g), hydration properties and adsorption capacity, has been assessed for different applications. For example, these minerals are used as soil conditioners to improve physical and chemical properties of soil, and reduce leaching of NO_3^- and $(PO_4)^{3-}$ from fertilizers, as primary sources of groundwater pollution (Malekian *et al*., 2011). Zeolite applications to soils can act as slow release fertilizers and increase water holding capacity, improving water and nutrient use efficiency (Nakhli *et al*., 2017). These minerals can also be raw materials for plant substrates, in particular as greenhouse media for the production of vegetables or as rooting media for cuttings of fruit and ornamental plants (Pond and Mumpton, 1985).

Zeolitites have not been significantly investigated for the control of plant diseases (De Smedt *et al*., 2015), but several studies have been carried out to investigate these materials for control of harmful insects (Kljajić *et al*., 2010; De Smedt *et al*., 2016; Rumbos *et al*., 2016; Floros *et al*., 2017). To our knowledge, there is no reported research on zeolitites for control of *B. cinerea* and *L. botrana* on grapevine.

Given the peculiar water sorbent capacity of zeolitites, due to their characteristic three-dimensional structures, the aim of the present study was to verify the effectiveness of a natural Italian chabasite-rich zeolitite, sprayed onto grapevines, for effects on grey mould and grapevine sour rot. These diseases are particularly harmful in high rainfall seasons. Sour rot is difficult to control (Hall *et al*., 2018), and is characterized by a typical smell due to the formation of ethyl acetate and acetic acid on infected grapevine bunches. This disease is caused by a complex of filamentous fungi, saprophytic yeasts, and bacteria (Steel *et al*., 2013). Given the positive results for zeolitites activity against insects, we also investigated their activity against grapevine moth. The study also analysed berries and wines from cv. Montepulciano vineyards to assess variations in composition, comparing the treatments of chabasite-rich zeolitites with those of synthetic fungicides and insecticides.

MATERIALS AND METHODS

Vineyard trial

Field trials were carried out in 2015 and 2016 in a vineyard located in Ari (Chieti province), and in 2017 in a vineyard located in Città Sant'Angelo (Pescara province), in the Abruzzo region of central Italy. The vineyard in Ari was established in 2001 and with the vines trained to the bilateral Guyot system, and with vine spacings of 2.5 × 1 m. The vineyard contained Montepulciano and Cococciola cultivars, each of approx. 5000 m², and both cultivars were on rootstock 1103 Paulsen. The vineyard in Città Sant'Angelo (CSA) was approx. 10,000 m² of cv. Montepulciano grafted on rootstock SO4, was established in 1989, and was trained to the Tendone system with vine spacings of 2.5 × 2.5 m. Both vineyards were located in grape growing areas usually subjected to epidemics of grey mould and sour rot and infestations of grapevine moth.

In both vineyards and in each of the 3 years of trials, the same experimental protocol was adopted. In each of the cultivars in the Ari vineyard, and in the CSA vineyard, trials were established to compare four treatments against grey mould with putative activity against sour rot, or three treatments against grapevine moth (Tables 1 and 2). Each treatment consisted of three replicates, each consisting of a plot of 162 m² in the Ari vineyard and 405 m² in CSA. Replicates were set up in randomized block designs.

In each of the three trials, an application strategy based on Italian chabasite-rich zeolitites (ICZ), (Agrisana s.r.l.) against grey mould, sour rot and grapevine moth, was compared with a strategy based on synthetic fungicides and insecticides (SYNT). A further treatment against grey mould and sour rot (SYNT/NAT) consisted of applications of the synthetic fungicides at pre-bunch closure followed by applications with zeolitites. In all the trials, untreated treatments were used as experimental controls (Tables 1 and 2). The zeolitites mineralogical composition (percent) was: Chabasite, 68.5 ± 0.9; Phillipsite, 1.8 ± 0.4; Analcime, 0.6 ± 0.3; K-feldspar, 9.7 ± 0.7; Mica, 5.3 ± 0.6; Pyroxene, 2.9 ± 0.4; and Volcanic glass, 11.2 ± 1.0. These zeolitites, collected from quarries in Sorano (GR), central Italy, were chosen for their high content in chabasite, and had high values of CEC (2.17 meq/g) and water retention (48.5 % p/p) (Malferrari *et al*., 2013).

Applications targeting grey mould were carried out before the occurrence of conditions favorable for infection, according to weather forecasts (Tables 1, 3 and 5). Only applications at pre-bunch closure were made according to the phenological growth stage and regardless of weather conditions. The pre-infection strategy was adopted taking into account the putative adhesion, persistence and rain resistance of zeolitites. In this way the preventive activity of the synthetic products was exploited, following current control guidelines.

In the Ari vineyard, rainfall, temperature and leaf wetness duration were recorded using an agrometeorological station (DigitEco s.r.l.), which was placed at the centre of the vineyard between the two cultivars (Table 3). In the CSA vineyard, meteorological data were obtained from a control unit (Hydrographic Service - Abruzzo Region) located about 6 km from the vineyard (Table 5). The meteorological data were used to verify the amount of rainfall and leaf wetness associated with the occurrence of infections.

The applications against *L. botrana* were carried out after the insect flight peak recorded in each vineyard from four pheromone traps, and after assessment of damaged berries (Table 4).

In all vineyards, at the berry pea-size growth stage, leaf removal at the bunch zone was carried out.

Table 1. Field applications against grey mould, sour rot and grapevine moth on cv. Montepulciano and Cococciola in the Ari vineyard in 2015 and 2016.

Application date	Growth stage	Treatment	Active ingredients	Application rate (kg/L ha^{-1})
30/06/2015	73	1 - SYNT	Spinosad	0.15
		2 - ICZ	Chabasite-rich zeolitite	15
		3 - SYNT/NAT	Chabasite-rich zeolitite	15
		4 - Untreated Control	Nil	-
24/07/2015	77	1 - SYNT	Cyprodinil + Fludioxonil	0.8
		2 - ICZ	Chabasite-rich zeolitite	15
		3 - SYNT/NAT	Cyprodinil + Fludioxonil	0.8
		4 - Untreated Control	Nil	-
06/08/2015	77	1 - SYNT	Pyrimethanil	2.5
		2 - ICZ	Chabasite-rich zeolitite	15
		3 - SYNT/NAT	Chabasite-rich zeolitite	15
		4 - Untreated Control	Nil	-
14/08/2015	83	1 - SYNT	Pyrimethanil + Chlorantaniliprole	2.5 + 0.27
		2 - ICZ	Chabasite-rich zeolitite	15
		3 - SYNT/NAT	Chabasite-rich zeolitite	15
		4 - Untreated Control	Nil	-
03/09/2015	85	1 - SYNT	Cyprodinil + Fludioxonil	0.8
		2 - ICZ	Chabasite-rich zeolitite	15
		3 - SYNT/NAT	Chabasite-rich zeolitite	15
		4 - Untreated Control	Nil	-
14/07/2016	75	1 - SYNT	Pyrimethanil + Spinosad	2.5 + 0.15
		2 - ICZ	Chabasite-rich zeolitite	15
		3 - SYNT/NAT	Chabasite-rich zeolitite	15
		4 - Untreated Control	Nil	-
28/07/2016	77	1 - SYNT	Cyprodinil + Fludioxonil	0.8
		2 - ICZ	Chabasite-rich zeolitite	15
		3 - SYNT/NAT	Cyprodinil + Fludioxonil	0.8
		4 - Untreated Control	Nil	-
04/09/2016	85	1 - SYNT	Cyprodinil + Fludioxonil	0.8
		2 - ICZ	Chabasite-rich zeolitite	15
		3 - SYNT/NAT	Chabasite-rich zeolitite	15
		4 - Untreated Control	Nil	-

All pesticide applications were carried out using pneumatic sprayers, with application volume of 500 L ha^{-1}.

Disease and insect assessments

The assessments of activity against grey mould were carried out in the Ari vineyard on October 2, 2015 and October 3, 2016, close to harvesting, which was done on October 4, 2015 and October 5, 2016. In the CSA vineyard the assessments were carried out on 29 September and 11 October, 2017. For each replicate of each treatment, 60 bunches located in the central rows of the vineyard plots were considered. The percentage of infected bunches (incidence), and the percentage of infected berries (severity), were determined.

The assessments of activity against the grapevine moth were carried out on equal numbers of bunches as follows: in the Ari vineyard, on July 14, 2015 and August 4, 2016 (2nd generation infestation), and on September 10, 2015 and September 30, 2016 (3nd generation infestation); in the CSA vineyard on July 30, 2017 (2nd generation infestation) and September 29, 2017 (3nd generation infestation). The percentage of damaged bunches (incidence), and the percentage of damaged berries (severity) were determined.

The activity of the synthetic fungicides and zeolitite applications on sour rot were assessed, in Ari and CSA

Table 2. Field applications against grey mould, sour rot and grapevine moth on cv. Montepulciano in the CSA vineyard in 2017.

Application date	Growth stage	Treatment	Active ingredients	Application rate (kg/L ha^{-1})
12/07/2017	75	1 - SYNT	Pyrimethanil	2.5
		2 - ICZ	Chabasite-rich zeolitite	15
		3 - SYNT/NAT	Chabasite-rich zeolitite	15
		4 - Untreated Control	Nil	-
23/07/2017	77	1 - SYNT	Cyprodinil + Fludioxonil	0.8
		2 - ICZ	Chabasite-rich zeolitite	15
		3 - SYNT/NAT	(Cyprodinil + Fludioxonil)	0.8
		4 - Untreated Control	Nil	-
09/09/2017	83	1 - SYNT	Pyrimethanil	2.5
		2 - ICZ	Chabasite-rich zeolitite	15
		3 - SYNT/NAT	Chabasite-rich zeolitite	15
		4 - Untreated Control	Nil	-
18/09/2017	85	1 - SYNT	Cyprodinil + Fludioxonil	0.8
		2 - ICZ	Chabasite-rich zeolitite	15
		3 - SYNT/NAT	Chabasite-rich zeolitite	15
		4 - Untreated Control	Nil	-

vineyards, at the same time as the grey mould assessments, calculating the percentages of infected bunches (incidence) and infected berries (severity).

Evaluations of effects of chabasite-rich zeolitites applications on grape yields

Field applications

In the CSA vineyard in 2017, the ICZ treatment plots were first examined for the activity of the applications and then further treated with zeolitites. Each of the three plots (replicates) of the ICZ treatment was subdivided into two 202 m^2 sub-plots. The six sub-plots were treated with zeolitites on 29 September, 15 d before harvest. Three of the sub-plots were not subjected to further applications (ICZ-A treatment). The other three sub-plots were further treated with zeolitites on 11 October, 2 d before grape harvest, which was carried out on 13 October (ICZ-B treatment).

Evaluation of yield and vinification

At harvest, in each of the sub-plots treated on 29 September (IZS-A treatment), or treated on 29 September and 11 October (IZS-B treatment), and in each of the three plots of the SYNT treatment, 12 plants were selected from central rows of each plot or sub-plot (four plants per row), and the grape yields were determined. Berries (100) from each of the plots or sub-plots, alternately taken from the wings, tips and centres of clusters located at about the mid-point along the vine-shoots, were collected. These berry samples were analysed for soluble solids (Brix), pH and total acidity, according to the methods of the Official Gazette of the European Communities. Regulation (EEC) No. 2676/90 (Official Journal L 272, 3.10.1990) (Table 6). A 100 kg sample from 12 plants of each of the three plots (SYNT treatment) or sub-plots (IZS-A and IZS-B treatments), was then vinified (three repetitions per treatment).

Each sample was crushed with a stalk-remover grape crusher. Approximately 93 kg of crushed grapes were obtained from each 100 kg sample. A traditional vinification for red wine was performed, with the cap of skins punched down three times per day. Thirty mg L^{-1} of sulfur dioxide, 20 g hL^{-1} of commercial dry yeast (after rehydration) and 20 g hL^{-1} of fermentation activators (diammonium phosphate + thiamine hydrochloride) were added at the beginning and again at half of the fermentation process. The fermentation ended after 15 d, the samples reached maximum temperature of 30°C during this period. Pressings were carried out to separate the solids after about 15 d, and the wines were decanted. At the end of this process, and for each sample, approx. 70 L of wine was obtained.

Chemical analyses of the wines

The wine obtained was analyzed at 3 months from racking to determine concentrations of the parameters

Table 3. Rainfall, temperature and leaf wetness periods on rainy days at the ARI vineyard in 2015 and 2016.

Date	Maximum temperature (°C)	Minimum temperature (°C)	Rainfall (mm d^{-1})	Leaf wetness (h d^{-1})
20/06/2015	20.3	13.2	4.2	3
24/06/2015	22.1	14.1	30.5	16
07/08/2015	25.1	20.6	75.1	10
15/08/2015	24.4	19.4	1.1	2
16/08/2015	23.6	17.6	40.3	16
04/09/2015	21.1	16.3	13.2	20
08/09/2015	26.2	19.2	0.5	2
19/06/2016	17.4	12.5	15.2	10
20/06/2016	18.3	12.3	0.6	2
23/06/2016	24.7	18.8	1.4	2
06/07/2016	23.7	20.0	0.8	3
09/07/2016	27.8	22.1	1.6	1
15/07/2016	14.6	12.8	100.8	19
16/07/2016	14.1	12.8	47.6	21
01/08/2016	24.7	18.8	14.2	7
23/08/2016	20.5	16.4	0.4	4
31/08/2016	21.6	18.8	1.2	8
05/09/2016	23.7	16.3	2.6	6
06/09/2016	17.2	12.6	22.6	12
07/09/2016	16.2	14.0	10.6	22
08/09/2016	19.2	14.4	0.2	9
09/09/2016	21.2	17.7	1.0	3
10/09/2016	21.2	17.6	0.4	3
11/09/2016	19.5	16.9	6.0	10
12/09/2016	20.7	17.1	0.8	7
16/09/2016	21.3	17.8	7.2	4
18/09/2016	18.8	15.4	0.6	3
19/09/2016	16.3	13.2	8.4	6
21/09/2016	17.2	14.9	2.0	5

Table 4. Numbers of grapevine moth adults captured in traps in two grape cultivars in the Ari vineyard in 2015 and 2016.

Survey data	Cv. Montepulciano		Cv. Cococciola	
	Trap A Capture number	Trap B Capture number	Trap A Capture number	Trap B Capture number
15/06/2015	15	12	11	15
22/06/2015	137	139	146	29
30/06/2015	18	33	77	14
07/07/2015	7	15	5	5
14/07/2015	1	1	4	2
21/07/2015	2	3	2	2
29/07/2015	5	8	4	0
05/08/2015	18	11	6	3
12/08/2015	35	36	44	26
18/08/2015	18	11	27	8
26/08/2015	11	8	8	4
02/09/2015	6	4	3	2
10/09/2015	2	2	0	0
18/09/2015	0	2	2	0
25/09/2015	1	2	1	1
01/10/2015	4	5	0	1
14/06/2016	0	0	0	0
21/06/2016	0	0	0	0
28/06/2016	0	0	0	0
05/07/2016	8	7	8	6
12/07/2016	47	45	33	35
19/07/2016	11	12	15	18
26/07/2016	7	6	8	8
02/08/2016	0	0	0	0
09/08/2016	0	0	0	0
16/08/2016	0	0	0	0
24/08/2016	3	4	2	3
30/08/2016	0	0	0	0
07/09/2016	0	1	0	1
14/09/2016	1	0	0	0
21/09/2016	0	0	0	0
28/09/2016	0	0	0	0

reported in Table 6. Analyses were carried out in accordance with the methods outlined in the official Gazette of the European Community, Regulation (EEC) No. 2676/90 (Official Journal L 272, 3.10.1990).

HPLC Analyses

Determination of anthocyanins in red wine samples, filtered through 0.45 µm nylon filters, was carried out according to OIV-MA-AS 315-11 Method (2007). Thirty microliters of each sample was analysed by HPLC. The chromatographic system was an HPLC Waters Alliance equipped with a Waters 2695 separation module connected to a Waters 2996 photodiode array detector. Separation of analytes was carried out using a Supelcosil LC18 column (5 µm particle size, 250 × 4.6 mm I.D.), as described in the OIV Method. The system was controlled by Waters Empower personal computer software. Identification of the anthocyanins, detected at wavelength 520 nm, was based on retention times. For the calibration curves, i.e. peak area versus concentration, malvidin-3-glucoside chloride (Sigma-Aldrich) was used, resulting in the linear range of concentration between 10 and 100 mg L^{-1}. The calculated regression line was used to compute the amount of each analyte in the samples by interpolation, using the external standard method.

Table 5. Rainfall, temperature and leaf wetness periods on rainy days of the CSA vineyard in 2017.

Date	Maximum temperature (°C)	Minimum temperature (°C)	Rainfall (mm d^{-1})	Leaf wetness (h d^{-1})
17/06/2017	27.1	20.1	4.8	8
28/06/2017	30.3	20.2	1.8	3
14/07/2017	30.2	22.2	39.8	10
24/07/2017	35.4	22.2	2.2	2
25/07/2017	29.4	20.3	13.6	22
10/09/2017	26.1	17.4	18.6	8
11/09/2017	24.5	18.3	21.6	18
19/09/2017	23.4	15.2	12.4	11
20/09/2017	16.3	12.1	10.1	10
24/09/2017	23.1	14.3	11.2	9
06/10/2017	13.3	10.1	11.6	9
07/10/2017	14.2	10.2	10.4	8

Statistical analyses

Statistical analyses were performed with the Tukey's honest significant difference (HSD) test, ($P = 0.05$), comparing each treatment, in each vineyard and year of trial, for the data of incidence and severity of grey mould, sour rot and grapevine moth. Tukey's honest significant difference (HSD) test, ($P = 0.05$) was also used to compare yield and wine data from each treatment.

RESULTS

Vineyard trial

Grey mould

In 2015, in the untreated controls for cv. Montepulciano in the Ari vineyard, mean grey mould incidence was 18.3% of the bunches, and mean severity was 1.2%. In the treated plants, mean incidence was from 0 to 1.1%, and mean severity was from 0 to 0.05%. Mean incidence and severity in treated plants were statistically different compared to the untreated control plants, but not between the different treatments (Table 7).

In 2015, in the cv. Cococciola in the Ari vineyard, mean incidence of *B. cinerea* infections in bunches of the untreated controls was 27.2% and mean severity was 1.4%. Both of these values were statistically different compared with those for the treated plants, which showed mean incidence from 0 to 1.7%, and mean severity from 0 to 0.06% (Table 7). As for cv. Montepulciano, no statistically significant differences were detected for the ICZ, ICZ/SYNT and SYNT treated plants (Table 7).

In 2016, in the Ari vineyard, infections were detected in the untreated controls of both cultivars, with mean incidence of 16.7% and mean severity of 0.4% in cv. Montepulciano, and of 56.1 and 3.7% in cv. Cococciola. Also in this case, all the treated plants had significantly reduced infections compared to the untreated controls, without significant differences of activity among treatments (Table 7).

In 2017, in the CSA Vineyard, no infections by *B. cinerea* were detected.

Sour rot

In 2015 in the Ari vineyard, the untreated controls of cv. Montepulciano had mean incidence of sour rot of 37.2% and mean severity of 6.0% (Table 7). In cv. Montepulciano, no sour rot was detected from the SYNT treatment which was statistically less than for the other treated plants, and the untreated control (Table 7). The ICZ and ICZ/SYNT treatments gave similar mean sour rot incidence (respectively, 7.8 and 7.2%) and mean sour rot severity (both at 0.7%). These values were statistically

Table 6. Chemical analyses of cv. Montepulciano berries and wines obtained from vines treated with either Italian chabasite-rich zeolitites or synthetic fungicides and insecticides for control of grey mould, sour rot and grapevine moth.

Parameter	Unit of measurement	Sample	Method of analysis
Total polyphenols *	mg L^{-1}	Wines	Folin-Ciocalteau
Total anthocyanins	mg L^{-1}	Wines	Spectrophotometric
Total acidity	g L^{-1}	Berries and wines	Acid/base titration
Soluble solids	° Brix	Berries	Fheling
pH 20°C	-	Berries and wines	Potentiometric
Ethyl alcohol	% vol.	Wines	Distillation
O.D. 420-520-620 (IC_3)	-	Wines	Spectrophotometric
Anthocyanins	mg L^{-1}	Wines	HPLC

* Total polyphenols expressed as gallic acid equivalents.

Table 7. Mean incidence and severity of different control strategies for control of grey mould and sour rot based on applications of Italian chabasite-rich zeolitites (ICZ), synthetic fungicides (SYNT) or zeolitites replaced by synthetic fungicide at pre-bunch closure (SYNT/NAT), in the cv. Montepulciano and Cococciola in the Ari vineyard.

Survey	Treatment	Grey mould				Sour rot			
		Cv. Montepulciano		Cv. Cococciola		Cv. Montepulciano		Cv. Cococciola	
		Incidence[a] (%)	Severity[b] (%)	Incidence (%)	Severity (%)	Incidence (%)	Severity (%)	Incidence (%)	Severity (%)
02/10/2015	1 – SYNT	0.00 a[c]	0.00 a	0.00 a	0.00 a	0.00 a	0.00 a	0.00 a	0.00 a
	2 - ICZ	1.11 a	0.05 a	1.67 a	0.05 a	7.78 b	0.74 b	1.11 a	0.07 a
	3 - SYNT/NAT	0.00 a	0.00 a	1.67 a	0.06 a	7.22 b	0.65 b	0.56 a	0.05 a
	4 - untreated control	18.33 b	1.19 b	27.22 b	1.37 b	37.22 c	5.99 c	8.33 b	0.71 b
03/10/2016	1 – SYNT	0.56 a	0.01 a	18.89 a	0.76 a	18.33 a	0.34 a	1.67 a	0.05 a
	2 - ICZ	1.11 a	0.01 a	20.56 a	0.90 a	18.33 a	0.41 a	2.22 a	0.04 a
	3 - SYNT/NAT	0.56 a	0.01 a	18.89 a	0.75 a	23.33 a	0.59 a	2.22 a	0.06 a
	4 - untreated control	16.67 b	0.44 b	56.11 b	3.74 b	55.56 b	2.49 b	10.00 b	0.29 b

[a] Incidence = percentage of infected bunches on the total number of bunches.
[b] Severity = percentage of infected berries on the total number of berries.
[c] Statistical analyses were performed according to Tukey's honest significant difference (HSD) test.
Different letters indicate significant differences ($P = 0.05$).

different compared to those from the untreated controls (Table 7). In cv. Cococciola, all the treatments gave similar and significantly lower values than the controls, in which mean incidence of sour rot was 8.3% and mean severity was 0.7% (Table 7).

In 2016, in the cv. Montepulciano at the Ari vineyard, mean incidence of sour rot in the untreated controls was 55.6% and mean severity was 2.5%. These were significantly greater than those from the other treatments, which did not differ significantly from each other (Table 7). In the untreated controls of cv. Cococciola at the Ari vineyard, mean sour rot incidence was 10.0% and severity was 0.3%. The other treatments gave mean incidence ranging from 1.7% to 2.2% and mean severity from 0.04 to 0.06% (Table 7).

In 2017, in the CSA vineyard, no sour rot was detected.

Grapevine moth

In 2015, after the flight peak of the second generation of *L. botrana* recorded on June 22, both cv. Montepulciano and Cococciola in the Ari vineyard were treated (Tables 1 and 4). In the assessment carried out on July 14, the untreated controls of cv. Montepulciano showed mean incidence of infestation of 33.3% and mean severity of 0.7% (Table 8). In the untreated controls of the cv. Cococciola, mean incidence of infestation was 45.0% and mean severity was 1.2% (Table 8).

Spinosad applied in the SYNT treatment at both vineyards gave complete control of the infestations in cv. Montepulciano, and low levels of infestation in cv. Cococciola at mean incidence of 2.2% and mean severity of 0.03% (Table 8).

The zeolitite applications decreased the grapevine moth infestations in both cultivars, to a lesser extent than in the SYNT treatment, but statistically different compared to the untreated controls (Table 8). In the ICZ treatment for cv. Montepulciano, mean incidence of infestation was 3.9% and mean severity was 0.05%. For cv. Cococciola mean incidence of infestation was 11.1% and mean severity was 0.17% (Table 8).

In 2015, applications with chlorantaniliprole were carried out 2 d after the grapevine moth flight peak of third generation adults recorded in both cultivars on 12 August (Tables 1 and 4). The mean incidence and severity of infestations (assessed on 10 September) in the untreated controls of cv. Montepulciano were, respectively, 8.3 and 0.19%, and for cv. Cococciola were, respectively, 27.8 and 0.7% (Table 8). The treatments with chlorantaniliprole and zeolitites, carried out in the SYNT and ICZ treatments, gave similar reductions of moth infestation, which were significantly different compared to the controls (Table 8).

In 2016, single applications of Spinosad in the SYNT treatment and zeolitites in the ICZ treatment were carried out in the Ari vineyard, on 14 July. These were against the second generation of *L. botrana*, after the peak of flights registered on 12 July (Tables 1 and 4).

Table 8. Activity of Italian chabasite-rich zeolitites (ICZ) and synthetic insecticides (SYNT) on grapevine moth bunch infestations in the cv. Montepulciano and Cococciola in the Ari vineyard in the surveys carried out at the 2nd moth generation: 14/07/2015 and 04/08/2016, and at the 3rd moth generation on 10/09/2015.

Treatment	14/07/2015		10/09/2015		04/08/2016	
	Incidence [a] (%)	Severity [b] (%)	Incidence (%)	Severity (%)	Incidence (%)	Severity (%)
Cv. Montepulciano						
1 – SYNT	0.00 a [c]	0.00 a	2.22 a	0.03 a	0.00 a	0.00 a
2 - ICZ	3.89 b	0.05 b	1.11 a	0.02 a	1.67 a	0.02 a
3 - untreated control	33.33 c	0.71 c	8.33 b	0.19 b	16.67 b	0.28 b
Cv. Cococciola						
1 – SYNT	2.22 a	0.03 a	1.67 a	0.03 a	2.22 a	0.03 a
2 - ICZ	11.11 b	0.17 b	6.11 a	0.11 a	4.44 a	0.07 a
3 - untreated control	45.00 c	1.17 c	27.78 b	0.68 b	15.00 b	0.28 b

[a], [b], [c], see Table 7.

Spinosad and zeolitite applications both significantly reduced the moth infestations compared to the controls (Table 8). In the untreated control, mean incidence of infestation was 16.7% in cv. Montepulciano and 15.0% in cv. Cococciola, while mean severity was 0.3% in both cultivars (Table 8). In the SYNT and ICZ treatments the mean incidence of infestation ranged from 0 to 4.4%, and mean severity from 0 to 0.07% (Table 8).

The low number of captures of third generation moth adults did not require further treatment applications in 2016 in the Ari vineyard (Table 4). During the assessment of 30 September, there was no additional damage compared to second generation moths.

In 2017, in the CSA vineyard and throughout the growing season, no insecticide applications were carried out because no moths were captured, or because there was only sporadic *L. botrana* presence (1–2 moths per trap). During the 30 July and 29 September assessments, no grapevine moth damage was found in the grapes.

Evaluations of effects of chabasite-rich zeolitite applications on yields

At harvest, no differences among treatments were detected in grape yield per plant (Table 9). Furthermore, compared to the SYNT treatment, the treatments with zeolitites (ICZ-A, ICZ-B) had no effects on accumulation of soluble solids or acidic balance of the berries.

The chemical composition of the wines obtained after 3 months of ageing is outlined in Table 10. Although the parameters of alcohol content, pH and total acidity did not vary among the treatments, the treatments gave statistically significant differences for concentrations of polyphenols and anthocyanins, and in wine colour intensity. Polyphenol content was significantly greater from the ICZ-A treatment (mean = 3213 mg L^{-1}) compared to SYNT (mean = 2922 mg L^{-1}), whereas the ICZ-B treatment gave the least amount (mean = 2475 mg L^{-1}). Concentrations of total anthocyanins in the three wines were also statistically different. The ICZ-A treatment gave greater anthocyanin content (mean = 625 mg L^{-1}) compared to the SYNT treatment (mean = 579 mg L^{-1}) and the ICZ-B treatment (mean = 486 mg L^{-1}). The concentration of anthocyanins affected the intensity of colour (IC_3), which resulted in an increased value from the ICZ-A compared to the SYNT treatment, while the ICZ-B treatment gave greater colour discharge (Table 10).

Table 9. Mean grape yields and grape composition parameters recorded in 2017 at harvest, for cv. Montepulciano vines in the CSA vineyard, treated with Italian chabasite-rich zeolitites (ICZ-A and ICZ-B) or synthetic products (SYNT).

Treatment	Yield (Kg $vine^{-1}$)	Soluble solids (° Brix)	pH	Total acidity (g L^{-1})
ICZ-A	10.0 a [a]	26.5 a	3.61 a	6.10 a
ICZ-B	9.8 a	26.5 a	3.61 a	6.10 a
SYNT	9.5 a	26.9 a	3.63 a	6.03 a

[a] Statistical analyses were performed according to Tukey's honest significant difference (HSD) test.
Different letters indicate significant differences (P = 0.05).

The composition of total anthocyanin fractions was determined, and the percentage of each glycosylated anthocyanin and the sum of acylated forms are outlined in Table 11. Montepulciano wines had characteristic anthocyanin profiles, with low amounts cyanidin gluco-

Table 10. Mean chemical composition values for Montepulciano d'Abruzzo wines obtained from cv. Montepulciano vines in the CSA vineyard, treated in 2017 with Italian chabasite-rich zeolitites (ICZ-A and ICZ-B) or synthetic products (SYNT), after 3 months of ageing.

Treatment	Ethyl alcohol (% vol.)	pH	Total acidity (g L^{-1})	Total polyphenols (mg $^{L-1}$)	Total anthocyanins (mg $^{L-1}$)	IC_3
ICZ-A	16.1 a[a]	3.65 a	5.93 a	3213 a	625 a	15.1 a
ICZ-B	16.1 a	3.67 a	5.93 a	2475 c	486 c	10.1 c
SYNT	16.3 a	3.67 a	6.03 a	2922 b	579 b	12.6 b

[a] See Table 9.

Table 11. Mean composition (%) of total anthocyanins in Montepulciano d'Abruzzo wines obtained from cv. Montepulciano vines in the CSA vineyard, treated in 2017 with Italian chabasite-rich zeolitites (ICZ-A and ICZ-B) or synthetic products (SYNT), after 3 months of ageing. Montepulciano d'Abruzzo total anthocyanins included glycosylate and acylated forms (sum of acetate and coumarate fractions).

Treatment	Delphinidin 3-G	Cyanidin 3-G	Petunidin 3-G	Peonidin 3-G	Malvidin 3-G	Acylated anthocyanins
ICZ-A	5.4 a[a]	0.5 a	9.3 a	9.6 a	58.0 a	17.6 a
ICZ-B	4.6 a	0.5 a	10.4 a	8.8 a	62.9 a	16.1 a
SYNT	4.6 a	0.5 a	8.8 a	9.0 a	60.2 a	17.4 a

[a] See Table 9.

side. The percentages of total glycosilated anthocyanins (delphinidin, cyanidin, petunidin, peonidin and malvidin), and of acylated anthocyanins (sum of acetates and coumarates) did not significantly differ among the different treatments. In particular, the glycosylated fractions were predominant, and malvidin 3-G was the major constituent in wine solution after 3 months of ageing.

DISCUSSION

Increasing awareness of the impacts of plant protection on the environment has led to restrictions on the use of synthetic pesticide products, with increasing research of predisposing epidemiological factors to diseases (Calzarano *et al*., 2018), and there has been increased research on environmentally-friendly products for disease and pest management (Calzarano and Di Marco, 2018). In the present study, Italian natural chabasite-rich zeolitites were evaluated as environmentally-friendly materials for management of grapevine grey mould, sour rot and grapevine moth.

In both years of trials carried out in the Ari vineyard, applications of zeolitites gave activity for grey mould control, which was comparable to that from synthetic fungicides. This activity was verified for applications of zeolitites against *B. cinerea* at all growth stages except the pre-bunch closure growth stage (Pearson and Goheen, 1988), and in the control strategy based only on applications of zeolitites.

The control strategies for *B. cinerea* were effective also against sour rot. The side activity of the anti-*Botrytis* fungicide mixture cyprodinil + fludioxonil against the sour rot is well known (Adaskaveg *et al*., 2011), but was greater than that from the zeolitite treatments only in 2015 in the cv. Montepulciano grapes.

However, the reductions of sour rot from the different control strategies was considerable in the presence of moderate infections, and to a lesser extent when the incidence of the disease was severe, as in 2016 in the cv. Montepulciano grapes.

The cv. Montepulciano and Cococciola have different susceptibilities to grey mould and sour rot. Severe infections of sour rot in cv. Montepulciano corresponded to minor grey mould infections. Similarly in cv. Cococciola, bunches heavily infected with *B. cinerea* were less affected by sour rot.

The activity of zeolitites against *L. botrana* was high, and was comparable to that of synthetic insecticides where mild infestations of the moth occurred. Zeolitites also gave good control of heavy infestations. This was for the second moth generation in 2015 in both cultivars in the Ari vineyard, but was less than that achieved from synthetic insecticides.

The lack of grey mould and sour rot in 2017 in the CSA vineyard could be ascribed to the dry weather conditions of that year, characterized by high temperatures and low relative humidity. Resistance to diseases in cv. Montepulciano clone could also result from the greater thickness of berry cuticles in this cultivar compared with others, despite the occurrence of rainfall predisposing to infections (Rogiers *et al*., 2005; Mundy, 2008). The absence of grapevine moth infestations in 2017 in the CSA vineyard may have also resulted from the high temperatures that occurred (Moosavi *et al*., 2017).

The good efficacy of the applications of zeolitites towards grey mould and sour rot could attributed to the physico-chemical properties of these materials (Bish and Ming, 2001; De Smedt *et al*. 2015). Water adsorption capacity and the resulting reduction in moisture in zeolitite-treated bunches could have caused the decreases in grey mould and sour rot (Ng and Mintova, 2008; Tatlier *et al*. 2018).

Applications of zeolitites lead to the formation of microscopic layers of mineral particles (Glenn and Puterka, 2005). High hydrophilicity of these layers of chabasite-rich zeolitites results in the absorption of condensing water and elimination of free water (Tatlier *et al*., 2018). Direct contact of disease inoculum with host tissues could be reduced by a physical barrier developed on the treated plant surfaces. This barrier can also reduce spore germination and prevent or hinder microbial growth (Walters, 2006).

Studies on the activity of zeolitites against grapevine moth are lacking, but the insecticidal potential of zeolitite formulations have been evaluated for control of others insect pests. These include stored-grain insects (Kljajić *et al*., 2010; Rumbos *et al*., 2016; Kavallieratos *et al*., 2018), *Tuta absoluta* on tomato (De Smedt *et al*., 2016) and bean weevil (Floros *et al*., 2017). These studies have demonstrated that zeolitites induced high adult and progeny mortality. Investigations on mechanisms of action towards different harmful insects have also been carried out for other mineral powders similar to zeolitites, such as kaolin, a clay mineral composed of aluminosilicate.

As in the case of kaolin, the epicuticles of insect larvae may be damaged by the non-sorptive particles of zeolitites for abrasion and by adsorption of epicuticular lipids to sorptive particles. Loss of water from the insect bodies leads to the death from desiccation (Ebeling, 1971; Glenn *et al*., 1999). This specific activity has recently been observed from applying zeolitites to Pharaoh ants (Van Den Noortgate *et al*., 2018). Plants treated with kaolin clay showed a low oviposition rates by different insects. Furthermore, hatch rate of eggs and larval development significantly decreased from these treatments, causing a high insect mortality (Puterka *et al*., 2000; Knight *et al*., 2000).

The larvae on which the mineral particles adhere can also die from starvation, because they are subject to tactile deterrence leading to inability to feed (Larenzaki *et al*., 2008). Deposition of the particle films on the treated plants can also reduce the visual cues for insects, and hinder recognition of plant parts on which the adults lay their eggs (Glenn *et al*., 1999; Mazor and Erez, 2004). The possible increases in infestations of insects not directly affected by kaolin applications (Knight *et al*., 2001; Markò *et al*., 2008) were not detected in the present study.

Zeolitite activity for control of grey mould, sour rot and grapevine moth has been linked with the adhesion and persistence of the mineral deposits on the treated grapes, with increased resistance to rainfall wash-off of the mineral. This characteristic is associated with the effectiveness of preventive control strategies against grey mould, based on applications carried out just before expected rainfall.

The use of zeolitites has also proved to be effective for integrated pest management for *L. botrana*. Applications were carried out immediately after the peak of adult insect flights, assessed as presence of penetration holes on grape berries (Amo-Salas *et al*., 2011).

One of the most interesting results from the present study is the possibility of using zeolitites to simultaneously control grey mould, sour rot and grapevine moth. This could provide a clear economic advantage for viticulturists, and for the environment, in a combined disease and pest management strategy that has not been previously suggested.

Increasing of temperatures, associated with climate change, could strongly influence the production of high quality grapes, affecting the grapevine development and phenology during growing seasons. It has been established, by focusing on phenolic compounds in black berry grapevine varieties, that high temperatures negatively affect colour intensity, resulting in poor colour wines (Buttrose *et al*., 1971; Kliewer and Torres, 1972; Mori *et al*., 2007). Recent studies on cv. Sangiovese showed that exposure of grape bunches to high temperatures lead to reductions in synthesis of anthocyanin, while anthocyanin degradation was stimulated (Movahed *et al*., 2016; Pastore *et al*., 2017a; Pastore *et al*., 2017b). Thus, in hot growing seasons as in 2017 in the CSA vineyard, the contents of phenolic compounds were low in all treatments compared to the usual amounts of these compounds in cv. Montepulciano grapes (Mattivi *et al*., 2006).

The timing of zeolitite applications to grapevine canopies influenced the concentrations of phenolic compounds in grape berries and wine, without affecting the percentage fraction of each individual anthocyanin. No differences resulted for alcohol contents and wine total acidity. When the last treatment with zeolitites was carried out no later than 15 d from harvest (treatment ICZ-A), the polyphenol concentrations increased and the wine developed increased colour intensity. This result is similar to that from foliar applications of kaolin, which is a radiation-reflecting inert mineral able to reduce leaf surface temperatures and influence major secondary metabolism pathways leading to biosynthesis of phenolic compounds and anthocyanins (Glenn and Puterka, 2005; Song *et al*., 2012; Conde *et al*., 2016). Dinis *et al*. (2016) showed that kaolin-treated grape berries had enhanced total amounts of phenols, flavonoids, anthocyanins and vitamin C compared with grapes from untreated vines. The timing of zeolitite applications was shown to be a crucial factor. Application close to grape harvest (the ICZ-B treatment) gave a residue of inert dust that effectively decreased the wine phenol contents, affecting anthocyanin concentration and colour intensity. This was probably due to the hydrophilic properties of zeolitites, determining the adsorption of target molecules (Perego *et al*., 2013; Mercurio *et al*., 2016; Lisanti *et al*., 2017). Recent studies have shown that natural and surfactant-modified zeolites are effective sorbents for removal of organic compounds such as phenol and 4-chlorophenol from aqueous solutions (Kuleyin, 2007; Yousef *et al*., 2011).

The low content of cyanidin glucoside associated with the high content of malvidin glucoside was attributed to the specific anthocyanin pattern of cv. Montepulciano (Mattivi *et al*., 2006), and to enzymatic conversion that occurred in berries during the late growing season (Versari *et al*., 1999).

Due to lack of interference of the grape composition, particularly for phenolic compounds, the use of zeolitites could further be encouraged.

The positive results obtained in this study need to be confirmed to fully assess the potential of zeolitites as environmentally-friendly control strategies for grapevine disease and pest management. Use of these compounds could also provide clear economic advantages for grape and wine production.

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