Effect of highly processed calcined kaolin residues on apple productivity and quality.

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ABSTRACT. Calcined kaolin-based particle films (PKPF) are effective in reducing insect, heat, photosynthetically active radiation (PAR) and ultraviolet radiation (UV) stress in plants due to the reflective nature of the heat-treated particles. The purpose of this study was to determine the effects of PKFP treatments applied at moderate (3%) and high rates (12% w/v) on apple physiology, yield and quality and the interaction with ambient ozone levels for a 6 year period. Fruit mass was increased by applications of PKPF at 3% and 12% in 4 of 6 years in non-irrigated treatments and in 2 of 6 years in irrigated treatments. Red fruit color was increased (lower hue angle) over the control in 5 of 6 years and in 2 of 5 years the 12% PKPF had improved red color

over both the 0% and 3% PKPF non-irrigated treatments. PAR interception over 6 years, adjusted for LAI, was greatest for the control, least for the 12% PKPF, and 3% PKPF was intermediate. Reduced PAR interception below the canopy was likely due to greater PAR reflection within the canopy. Whole canopy temperature was significantly higher for the control (26 °C) and lower for the 3% and 12% PKPF treatments (24°C). Fruit mass increased in the PKPF treatments, relative to the irrigated control treatment (%), with increasing maximum ozone levels during May. In laboratory studies, ozone degradation was greatest for alfalfa, least for calcined kaolin and the addition of alfalfa to calcined kaolin increased degradation proportionately. The present study confirms that calcined kaolin is an effective catalyst for ozone degradation and organic materials, such as alfalfa, are even more effective, due to the direct reaction with carbon molecules. Whole canopy gas exchange measurements (1000 to 1600 HR) over a 10 day period in 2011 indicated that the 2.7% PKPF+0.3% alfalfa dust consistently had higher photosynthesis, 0.3% alfalfa was intermediate, while the control and 3% PKPF had the lowest photosynthesis rate. Whole canopy ozone degradation indicated that the 2.7% PKPF+0.3% alfalfa dust consistently had the greatest ozone degradation, 3% PKPF and 0.3% alfalfa were intermediate and the untreated control had the least ozone degradation. There is evidence that the 0.3% alfalfa stimulated a small amount of microbial growth on the leaf surface while the 2.7% PKPF+0.3% alfalfa stimulated a much greater amount of microbial growth. This synergistic effect may be due to the increased surface area in the particle film providing habitat for microbial populations and the reflection of UV by the particles that can be deleterious to microbial growth within that habitat. Data support the concept that chronic ozone damage is moderated to a significant degree by the use of surface treatments that catalyze ozone

degradation in a particle film. The use of PKPF may be one tool to mitigate not only increased ozone stress but also heat stress from increased growing season temperatures in the future.

1. Introduction

Kaolin-based particle films, specifically processed calcined kaolin (PKPF), have utility in reducing insect, heat, photosynthetically active radiation (PAR) and ultraviolet radiation (UV) stress in plants due to the reflective nature of the heat-treated particles (Glenn and Puterka, 2005). The particle film changes the plant's leaf/fruit texture and the reflected light signature of the plant resulting in deterrence of many pest insects. (Glenn and Puterka, 2005; D'Aquino et al. 2011; Leskey et al. 2010; Pascual et al. 2010; Sackett et al. 2007). The particle film alters reflected infrared (IR), PAR, and UV radiation compared to an untreated plant (Glenn et al., 2002).

Reflection of IR reduces canopy temperature and, consequently, potential transpiration (Boari et al., 2015; Glenn, 2010; Jifon and Syvertsen, 2003; Mofteh and Al-Humaid, 2005; Steiman et al., 2011). The reflection of PAR by the particle film at the leaf level is compensated in varying degrees by diffusion of PAR into the interior of the canopy (Glenn and Puterka, 2007; Rosati et al., 2007; Wünsche et al. 2004). The combined particle film effects of reduced canopy temperature and increased diffusion of PAR into the interior of the canopy can increase whole canopy photosynthesis (Glenn et al. 2003; Glenn, 2009 and 2010) or have no effect (Wünsche et al. 2004). The effect of PKPF on yield studies is similarly inconsistent. Excluding sunburn effects, many studies show increased yield and fruit quality of horticultural crops (Aly et al., 2010; Glenn, 2009 and 2010; Glenn and Puterka, 2007; Glenn et al. 2001, 2003 and 2005; Lapointe et al. 2006; Cantore et al. 2009; Pace et al. 2007; Wand et al. 2006; Saavedra et al.

2006; Steiman et al. 2007; Boari et al. 2014; Ergun, 2012; Khaleghi et al. 2015; Lalancette et al. 2005; Shellie and Glenn, 2008; Shellie and King, 2013; Sugar et al., 2005; Srinivasa Rao, 1985). There are also studies demonstrating no or negative effects of PKPF on fruit yield and quality (Schupp et al., 2002; Gindaba and Wand, 2005; Kahn and Damicone 2008; Lombardini et al. 2005; Russo and Diaz-Perez, 2005). Based on the methods of these studies it is most likely that the particle film residue density ranged from 1 to 4 g·m⁻² based on application rates ranging from 12 to 50 kg/ha or 1.5 to 6% (w/v).

Jones (1963) demonstrated that hydrous kaolin (kaolinite) provided slight protection of tobacco from ozone damage but charcoal and diatomaceous earth resulted in almost complete protection from ozone damage. Charcoal has a very high surface area (674 m²/g (Dunicz, 1961); diatomaceous earth has moderate surface area (21 m²/g Tsai et al., 2006) and the calcination process that dehydrates kaolinite reduced the surface area from 19 to 17 m²/g (Plešingerová, et al. (2011). Charcoal degrades ozone upon contact; the carbon is oxidised to carbon monoxide and carbon dioxide, resulting in destruction of the ozone molecule. (Deitz and Bitner , 1973). Glenn et al. (2015) have demonstrated that the mass of microbial DNA extracted from leaf surfaces is linearly related to the amount of kaolin residue on the leaf surface and the amount of microbial DNA on kaolin treated leaves is 2-5 times greater than untreated control treatments. According to Jones (1963) inert particulate materials serve as catalysts to degrade ozone in an exothermic reaction. Therefore both carbonaceous materials, such as microbial mass, and inert particulates, such as kaolin and other clay materials, can degrade ozone to some extent. Leaf surface microbial growth is limited by the resources available to the organisms from the leaf and the environmental conditions of the leaf. PKPF is highly reflective of UV radiation which

provides a reduced UV habitat in addition to increased surface area for microbial colonization. Nutrients are limiting for microbial growth and addition of low carbon:nitrogen (C:N) materials, such as alfalfa powder, may provide nutrients to increase microbial growth and further increase ozone degradation at the leaf surface.

The purpose of this study was to determine the effects of highly processed calcined kaolin particle film residues applied at higher rates (12% w/v) than generally documented and infer the mechanisms of action. The role of ozone degradation was also investigated in the yield and quality response of apple to PKPF applications by adding alfalfa powder to field studies to evaluate the effect of a highly biodegradable material with a low C:N ratio on microbial growth and ozone degradation.

2. Methods and Materials

2.1 Field plots and treatment application

The apple orchard was a moderate density planting ($500 \cdot \text{ha}^{-1}$) of 'Empire'/'Malling7A' planted in 1992 at the USDA/ARS Appalachian Fruit Research Station, Kearneysville, WV. Tree water requirements were based on 70% of pan evaporation (Glenn, 1995, 1999). Irrigation treatments consisted of two drip emitters per tree providing the daily water needs. Treatments were randomly assigned in 2005 in a split-plot block design with irrigation as the main plot and PKPF treatment as the subplot with six, two tree replicates. In all years, the trees were hand-thinned post-bloom. Trees received a PKPF treatment or were not treated. All treatments were over-sprayed with conventional pesticides to protect from disease or insect damage. Conventional orchard practices were used in tree training, mowing, nutrition, and weed control.

Apple trees received applications of a highly reflective, white, calcined hydrophilic particle based on kaolin mineral (PKPF treatment was Surround WP™, NovaSource, a division of Tessenderlo Kerley Inc. Phoenix, AZ) in addition to a conventional pesticide spray program. The mineral was processed to a bright white color of > 90% reflectance, with mean particle size <2 µm in diameter. PKPF was applied at the rate of 25 kg/ha and 100 kg/ha for 3% and 12% (w/v) during the 2005-2010 growing seasons. The PKPF treatments were applied in a spray volume of 833 L·ha⁻¹ (approximately 50% of tree row volume) using an air blast sprayer at a ground speed of 3.2 km/hr. There was an untreated control treatment. PKPF treatments were applied every 2 weeks following petal fall until 2 to 3 weeks before harvest.

In 2011 and 2012 new treatments were randomly assigned in a split-plot block design with irrigation as the main plot and PKPF treatment as the subplot with four double-tree replicates (3% w/v PKPF, 2.7% w/v PKPF + 0.3% w/v alfalfa powder (Now Foods, Bloomingdale, IL; C:N = 18:1), 0.3% w/v alfalfa powder or untreated). Trees were managed as before except that summer pruning was conducted in 2012 and the pruning weights determined.

2.3 Field measurements

At harvest, all fruit were weighed and counted for each tree in a plot. Fruit from each tree were processed with an electronic grader that counted and weighed each fruit. Ten fruit were subsampled and the hue angle measured on 4 sides around the equator of the fruit for 2005-2010.

Canopy light transmission was measured using two 1-m light bars (LI191SA; Licor, Lincoln, NE). Canopy light transmission within 1 hour of solar noon was measured by placing the reference sensor horizontally in an open area and placing the analysis sensor horizontally beneath the tree. Four measurements within the shadow of the tree were recorded. These data were collected once in each year (2005-2010). Following harvest, the trees were covered with a netting to capture all the leaves when they abscised. The leaves were collected and air-dried at 70 °C for approximately 1 week. At sampling, a subsample of approximately 3 kg fresh weight was separated, leaf area was measured, and the ratio of air-dried weight:leaf area calculated. This ratio was used to convert the total air-dried weight of each tree to total leaf area. Leaf area index (LAI) was the quotient of the total leaf area divided by the area of the canopy shadow measured within one hour of solar noon.

The residue on leaf samples was measured in **August and September** 2005-2010 with the exception of 2006 **preceding re-application**. Ten leaves per tree were detached for measurement. Pre-weighed tissue paper was wetted and used to wipe the upper and lower surfaces until no residue was visible. The pre-weighed tissues were air dried and the added weight of the leaf residue determined. The leaf residue mass was divided by the leaf area of the combined 10 leaves. Data were collected across the PKPF treatments and pooled over irrigation treatments. In 2011 and 2012, 10 leaves per tree were washed with sterile water and sonicated to extract the surface residue and microflora according to Glenn et al. (2015). The residue amount and DNA content of the residue were determined following Glenn et al. (2015). The DNA content of the alfalfa powder was determined using the same procedures (Glenn et al., 2015).

Whole canopy temperature was measured in August 2008 using an infrared imaging camera (Model A-20, FLIR, Wilsonville, Oregon). Images were collected at 1400-1500 HR under clear sky conditions with maximum illumination of the canopy. The outline of the canopy was defined using Researcher software (version 2.9, FLIR, Wilsonville, Oregon) and the mean temperature of the canopy determined for individual trees.

Whole tree gas exchange and ozone degradation were measured in open-top chambers in 2011 similar to Glenn (2010). The whole canopy chamber was constructed of 0.762- mm-thick polycarbonate (Makrolon GP; Sheffield Plastics Inc.- Bayer Material Sciences Pittsburgh, PA) in a rigid cube 2.4 x 2.4 x 2.4 m. A framed polycarbonate pitched roof covered the cube and the floor was a polyethylene tarp material split to the center to slide onto the tree and was sealed with a Velcro strip.

Air was forced into each chamber with a one horsepower fan attached to a metal conduit with a cross-sectional area of 777 cm². Five holes were drilled in the conduit to measure air velocity with a velometer (Model 8346, TSI Inc. Shoreview, MN) and 10 2.5 cm positions at each sample port were measured at the beginning and end of the sampling period. Velocity data were averaged to calculate mass air flux. Air was forced into the chamber from below the chamber through a diffusion grate located 50 cm from the tree trunk. Leaf movement was visually assessed to insure no large eddies developed in the chamber. Approximately 6 chamber volumes were exchanged per minute and this air flow maintained internal air temperature 1 to 2 °C above ambient. Air temperature was measured with a shielded thermocouple hanging approximately 30 cm into the chamber through the outlet port. Whole canopy net CO₂ and H₂O exchange were

measured with an infrared gas analyzer (IRGA) (CIRAS-1, PP Systems, Haverhill, MA) from the difference in CO₂ and H₂O concentration between the inlet (reference) and the outlet (analysis) ports of each chamber. Equal lengths of tubing were inserted into the conduit and the outlet port, and the sampled air was drawn to the IRGA with a pump. Response time was 5-10 s. The sampled air was blown into a cylinder that was sampled by the IRGA with its own sampling pumps. Multiple chambers were sampled sequentially at 1 min intervals using a programmable controller (SDM-CD16AC, Campbell Scientific, Logan, UT) that controlled solenoid valves on the reference and analysis tubes of each chamber. The controller was programmed and data collected with a datalogger (CR-7, Campbell Scientific). Ozone concentration was measured using two dual beam ozone monitors (Model 205; 2B Technologies, Boulder, CO) in a parallel system that operated simultaneously with the gas exchange system. The ozone monitoring tubing was a Polytetrafluoroethylene (PTFE, Teflon™) tubing to minimize degradation and all tubing lengths were equivalent. In addition to chambers enclosing the trees, and empty chamber and ambient air at 2 m were sampled. The empty chamber provided the system degradation amount and the air sample was the ambient ozone level in addition to providing a reference to equilibrate the reference and analysis ozone monitors.

Diurnal data were collected Aug 23 to 1 Sept. 2011. During each sampling, two trees of each treatment were simultaneously measured for 2 to 3 d. The chambers were moved to two other trees within the treatment providing four single tree replications of whole tree gas exchange. Photosynthetically active radiation (PAR), relative humidity, wind speed, pan evaporation, and air temperature were measured at a weather station approximately 500 m from the measurement site. Data were collected for 24 h each day but only data from 1000 to 1600 HR, were analyzed.

PKPF treatment effects were analyzed over days and hours using analysis of covariance in which PAR, LAI and vapor pressure deficit (VPD) were the independent covariates. Data were analyzed using SAS (version 8). Adjusted treatment means were compared using PDIFF which compares least squares means from the analysis of covariance. Treatment means were compared using Fisher's protected least significant difference (LSD), $P \leq 0.05$.

2.3 Laboratory measurements

In laboratory studies, the degradation of ozone by calcined kaolin, alfalfa and their combination was measured in flow-through systems. A 2 cm X 12 cm PTFE coated wire 100 mesh platform (Part # 100X100S0045W36_PTFE; TWP Inc. Berkeley, CA) was placed inside a 2 cm X 15 cm tube in which a calibrated ozone stream (Model 306; 2B Technologies, Boulder, CO) of 100 ppb ozone was passed over and under the platform. The outgoing stream was measured with a calibrated ozone monitor (Model 205; 2B Technologies, Boulder, CO). The data are expressed as the percentage degradation relative to the untreated platform. The particle density was determined by weighing the platform before and after treatment application and dividing by the area of the platform.

3. Results and Discussion.

3.1 Yield and quality responses

Fruit mass was increased by applications of PKPF at 3% and 12% in 4 of 6 years in non-irrigated treatments and in 2 of 6 years in irrigated treatments. In 2010 Non-irrigated 12% PKPF was significantly greater than control both irrigated and non-irrigated and all other treatments were intermediate (Table 1).

Red fruit color was increased (lower hue angle) over the control in 5 of 6 years and in 2 of 5 years the 12% PKPF had improved red color over both the 0% and 3% PKPF non-irrigated treatments (Table 2). Increasing the particulate residue on fruit and increasing red color are intuitively contradictory responses; red color generally increases with increasing incident PAR at the fruit surface, however, previous reports have confirmed this response (Aly et al., 2010; Ergun, 2012; Glenn et al. 2001, 2003 and 2005; Glenn and Puterka, 2007). There are no studies on ozone effecting apple color development but a possible mechanism for the increased red color is the degradation of ambient ozone throughout the growing season. Support for this hypothesis is increased red color for 2 of 5 years in the 12% PKPF compared to the 0% and 3% PKPF non-irrigated treatments in which there would be greater particulate residue and greater microbial biomass potentially resulting in greater ozone degradation at the fruit surface.

PAR interception varied over the 6 years due to variation in LAI of the individual trees. PAR interception over 6 years, adjusted for LAI, was greatest for the control, least for the 12% PKPF, and 3% PKPF was intermediate (Table 3). Reduced PAR interception below the canopy was likely due to greater PAR reflection within the canopy (Glenn and Puterka, 2007) and a contributing mechanism for the improved red fruit color in the 3% and 12% PKPF treatments. Rosati et al. (2006) modeled walnut and almond canopy light distribution of PKPF treated trees. They found that PKPF increased incident PAR within the interior canopy over untreated which is confirmed in this study (Table 3). Their modeling work also predicted a 9% increase in canopy photosynthesis in PKPF treated trees due to the improved light distribution and the present study demonstrates that this increased photosynthesis can be effectively partitioned to fruit sinks.

3.2 Canopy responses

Whole canopy temperature was significantly higher for the control (26 °C) and lower for the 3% and 12% PKPF treatments (24°C). There were no differences between the 3% and 12% PKPF treatments under ideal measurement conditions of clear sky and high illumination of the canopy at mid-afternoon. The 2°C reduction of canopy temperature is typical of data for the mid-Atlantic climate (Glenn et al., 2003; Glenn, 2009) and probably represents the maximum cooling potential for these environmental conditions with low to moderate VPD's (Jackson, 1982).

Leaf residue levels ranged from 0.4 to 2.8 g/m² in the control, 1.5 to 3.5 in the 3% PKPF and 3.7 to 8.2 in the 12% PKPF treatments (Table 4). The control residue is due to natural dust accumulation and varies due to rainfall frequency that washes away the dust. The 3% PKPF residue levels are similar to other published data (Jifon and Silversyn, 2003) and the 12% PKPF did achieve higher residue levels and demonstrated that higher residues can be developed in a summer rainfall climate despite frequent and heavy rainfall.

3.3 Ozone response

The increase in fruit mass (Table 1), relative to the irrigated control treatment (%), was positively correlated with maximum ozone levels during May but not correlated with May mean temperatures or maximum temperatures in May for 2005-2010 (Figure 1) or any other monthly mean temperature, maximum temperature or monthly ozone level (data not presented). Early publications in particle film technology (Glenn et al 2005) demonstrated that particle film applications in May (Kearneysville, WV) and or June (Wenatchee, WA) were the key times for PKPF applications to increase apple mass. This time period coincides with rapid cell division in

developing fruit (Goffinet et al., 1995). It was interpreted in Glenn et al. (2005) that the reduction in canopy temperature and heat stress from the PKPF treatments in May and June were the primary mechanisms increasing fruit mass due to increased cell division and sink size. However, data from the present study also suggests that PKPF is reducing chronic ozone damage at a key developmental stage in apple production. Retzlaff et al., (1991) demonstrated a linear negative photosynthesis response of young apple trees to ozone levels as low as 30 ppb, similar to levels in the present study.

3.4 Laboratory responses

In laboratory studies, ozone degradation was greatest for alfalfa, least for calcined kaolin and the addition of alfalfa to calcined kaolin increased degradation proportionately (Figure 2). Ozone is degraded by double bonds (Lewis and Gagg, 2010) and thus reacts with surfaces having double bonds, most notoriously, rubber and rubber products but also organic materials and divalent metals (Jones, 1963), hence the surface damage caused by ozone pollution. Ozone degradation is an exothermic reaction and causes leaf burn and tissue damage at high levels. Jones (1963) screened a range of organic and inorganic materials to identify particulate materials that could be effective catalysts to degrade ozone not in direct contact with the plant surface. He found that kaolin, presumably hydrous kaolin (kaolinite), not calcined kaolin (PKPF), reduced ozone damage in *Nicotiana glutinosa*. Highly reactive materials such as diatomaceous earth, charcoal and Fe_2O_3 provided the greatest reduction while kaolin and Tulare clay were intermediate. The present study confirms that calcined kaolin is an effective catalyst for ozone degradation and organic materials, such as alfalfa, are even more effective, similar to charcoal (Jones, 1963) due to the direct reaction with carbon molecules. These particle films have a very high surface to volume ratio making them effective at the plant surface level and preventing both the surface

interaction that burns the leaf with the exothermic reaction but also ozone uptake through the stomata. Diphenylamine (DPA) and Wilt Pruf™ (**di-1-p-menthene**) have also been shown to reduce ozone damage (Elfving et al., 1976).

3.5 Whole canopy gas exchange and ozone responses

Whole canopy gas exchange measurements (1000 to 1600 HR) over a 10 day period in 2011 indicated that the 2.7% PKPF+0.3% alfalfa dust consistently had higher photosynthesis, 0.3% alfalfa was intermediate, while the control and 3% PKPF had the lowest photosynthesis rate (Figure 3). Previous reports have demonstrated no or increased whole canopy photosynthesis for short duration studies using 3% PKPF (Glenn, 2009 and 2010; Glenn et al., 2003; Wünsche, et al., 2004).

Whole canopy ozone degradation indicated that the 2.7% PKPF+0.3% alfalfa dust consistently had the greatest ozone degradation, 3% PKPF and 0.3% alfalfa were intermediate and the untreated control had the least ozone degradation (Table 5). In previous work Glenn et al. (2015) demonstrated that the use of PKPF increased microbial growth on apple leaves 2 to 5 fold over untreated leaves. 0.3% Alfalfa powder was applied with 2.7% calcined kaolin to provide C and N to further stimulate microbial populations on the leaf surface and increase the organic matter that could catalyze ozone degradation. This hypothesis proved true since both 0.3% alfalfa and 2.7% PKPF+0.3% alfalfa powder had greater ozone degradation than the control and the 2.7% PKPF+0.3% alfalfa powder had greater ozone degradation than 3% PKPF alone (Table 5).

3.6 Treatment and leaf residue interactions

DNA(mg)/m² leaf area was linearly related to the recovered residue mass similar to Glenn et al. (2015). The control, 2.7% PKPF+ 0.3% alfalfa, and alfalfa treatments had a significantly greater slope than the 3% PKPF alone based on analysis of covariance using the residue mass/leaf area as the independent covariate (Figure 4).

The following is a hypothetical calculation using Figure 4 mean data:

The mean control residue mass is 1.84 g/m² and the mean 0.3% alfalfa residue mass is 2.00 g/m² (mean of treatment data points in Figure 4) indicating an increase of 0.16 g/m² due to the deposition of alfalfa alone.

Based on the slope of 14.025 in Figure 4, the addition of 0.16 g/m² of alfalfa residue at any residue mass/leaf area would contribute an additional 2.24 mg DNA/m² (14.025 x 0.16). The mean alfalfa residue mass contains 8.22 mg DNA/g of residue adding 1.32 mg DNA to the residue (8.22 x 0.16). This calculation indicates that microbial DNA may account for an additional 0.52 mg DNA/m² (1.84 - 1.32 mg DNA/m²) in the 0.3% alfalfa treatment.

Examining the relationship between 3% PKPF and 2.7% PKPF+0.3% alfalfa at a residue density of 3 g/m² indicates that 3% PKPF would have 13.1 mg DNA/m² and 2.7% PKPF+0.3% alfalfa would have 30.3 mg DNA/m² based on the regression equations (Figure 4), respectively. However, the alfalfa and the associated microbial biomass is predicted to only contribute 2.24 mg DNA/m² not 17.2 (30.3-13.1) so the additional DNA likely is due to increased microbial growth stimulated by the alfalfa and PKPF combination. Therefore, there is evidence that the 0.3% alfalfa stimulated a small amount of microbial growth on the leaf surface (0.52 mg

DNA/m²) while the 2.7% PKPF+0.3% alfalfa stimulated a much greater amount of microbial growth (17.2 mg DNA/m²). This synergistic effect may be due to the increased surface area in the particle film providing habitat for microbial populations and the reflection of UV by the particles that can be deleterious to microbial growth within that habitat.

3.7 Yield responses

In 2011, fruit were inadequately thinned and a heavy and excessive crop load developed. The 2.7% PKPF+0.3% alfalfa treatment had the highest crop load, 0.3% alfalfa and 3% PKPF were intermediate and the control had the lowest crop load (Table 6). The 2011 data suggest that all treatments enhanced photosynthesis and consequently fruit retention and subsequent crop load compared to control since there was no significant difference in mean fruit mass. The increase in crop load is likely the result of increased photosynthesis during the first 6 weeks of fruit development when fruit drop is determined by source strength and photosynthesis (Goffinet et al., 1995; Greene et al., 2013).

In 2012, as a result of the excessive crop in 2011, there was a reduced fruit crop load. Trees were summer pruned as a result of the low crop load initiating excessive vegetative growth. There were no treatment differences in summer pruning fresh weight. There were differences, however, in the relationship between fruit number and fruit mass in which the 0.3% alfalfa treatment had the largest fruit mass, adjusted to fruit number, 2.7% PKPF + 0.3% alfalfa was intermediate and the 3% PKPF and control had the lowest fruit mass adjusted to fruit number (Table 6). The 0.3% alfalfa treatment is virtually invisible and does not increase the reflective nature of the canopy as does the PKPF treatment. These data again support the concept that

chronic ozone damage is moderated to a significant degree by the use of surface treatments that catalyze ozone degradation in a particle film.

4. Conclusion

When this study was initiated in 2005, it was expected that a 12% PFPK treatment would be an excessive leaf residue and fruit covering, therefore, reducing photosynthesis, yield and fruit size and fruit color. However, the data did not support that expectation over 8 years of study. While yield was not increased or decreased by high residue application of PKPF at 12% compared to 3% PKPF, improved fruit color was likely due to increased intra-canopy reflection and perhaps enhanced ozone degradation. Some studies document reduced apple color (Schupp et al., 2002) with PKPF treatments and some studies find no increase in yield (Gindaba and Wand, 2005; Kahn and Damicone 2008; Lombardini et al. 2005; Russo and Diaz-Perez, 2005). It is the author's experience that the application technique can significantly alter the characteristics of the particle film and the subsequent response. As noted in the methods, a tractor speed of 3.2 km/hr is used which is in contrast to a more typical commercial speed ≥ 8 km/hr or hand-gun application which do not create a uniform particle film on plant surfaces but rather a spotty coverage with extremely dense depositions and voids in-between the spots. Visual examples of poor coverage (New York Fruit Quarterly Spring 2002 ; <http://www.nyshs.org/pdf/fq/02spring/spring02.pdf>) and uniform film coverage (Agricultural Research Magazine, November 2000; "Whitewashing Agriculture"; <http://www.ars.usda.gov/is/AR/archive/nov00/white1100.htm>) are found in popular trade magazines. If a uniform particle film is developed, higher residues may improve fruit quality without a reduction in photosynthesis if economically justified. An added benefit of PKPF

treatment is the potential mitigation of chronic ozone damage. The calcined kaolin particles alone catalyze the degradation of ozone but the stimulation of microbial populations on the leaf surface due to the particles (Glenn et al. 2015) may further aid in ozone degradation on plant surfaces. Ozone levels are positively related to air temperature and the expected increase in growing season temperatures associated with climate change will result in greater ozone levels in the future although the amount is unknown at this time (Meehl, et al., 2007; Vingarzan, 2004). The use of PKPF may be one tool to mitigate not only increased ozone stress but also heat stress from increased growing season temperatures in the future.

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Table 1. Mean fruit weight for calcined kaolin particle film (PKPF) and irrigation treatments over a 6-year period at Kearneysville, W Va. ‘Empire’ apple.

Treatment	Irrigation	Mean fruit weight (g/fruit)					
		2005	2006	2007	2008	2009	2010
Control	Irrigated	132 a ^z	114 b	110 b	134 a	132	128 b
3% PKPF	Irrigated	134 a	122 a	126 a	131 a	138	138 ab
12% PKPF	Irrigated	133 a	123 a	128 a	128 a	134	135 ab
Control	Non-irrigated	123 b	111 b	102 b	117 b	138	128 b
3% PKPF	Non-irrigated	138 a	120 a	126 a	131 a	134	132 ab
12% PKPF	Non-irrigated	134 a	122 a	123 a	128 a	138 ns	140 a

^z Adjusted means are estimated from analysis of covariance using number of fruit per tree as the independent covariate and mean separation within years utilizing SAS (version 8.0, SAS, Cary, NC) Proc PDIFF at $P \leq 0.05$.

Table 2. Mean hue angle for calcined kaolin particle film (PKPF) and irrigation treatments over a 6-year period at Kearneysville, W Va. ‘Empire’ apple. (The lower the hue angle value, the redder the fruit)

Treatment	Irrigation	Hue angle (degrees)					
		2005	2006	2007	2008	2009	2010
Control	Irrigated	71 a	65 a	74 a	72 a	58 a	77ab
3% PKPF	Irrigated	50 b	57 b	50 b	48 b	48 b	68b
12% PKPF	Irrigated	54 b	51 b	53 b	40 c	46 b	74ab
Control	Non-irrigated	71 a	64 a	75 a	68 a	57 a	87a
3% PKPF	Non-irrigated	46 b	55 b	53 b	50 b	42 b	73ab
12% PKPF	Non-irrigated	53 b	43 c	46 c	38 c	43 b	71ab

^z Mean values within a column followed by the same letter are not significantly different ($P=0.05$) based on Ryan-Einot-Gabriel-Welsch multiple F test.

Table 3. Interception of photosynthetically active radiation at solar noon in 6 treatments over 6 years in Kearneysville, WV.

		Interception (% of full sun)						Overall mean
PKPF		August	September	October	July	July	October	
(%)	Irrigation	2005	2006	2007	2008	2009	2010	
0	Irrigated	93	86a ^z	82a	94a	95	95a	91a ^y
3	Irrigated	94	87a	82a	93a	96	92b	90ab
12	Irrigated	91	86a	79a	90b	95	85c	87b
0	None	93	82b	76b	94a	96	95a	
3	None	93	79b	74b	93a	94	93b	
12	None	91	83b	77b	89b	95	86c	
		ns ^x			ns			

^z Mean values within a column followed by the same letter are not significantly different ($P=0.05$) based on Ryan-Einot-Gabriel-Welsch multiple F test.

^ySignificantly different at $P=0.10$ based on analysis of covariance using LAI as the covariate over irrigation treatments utilizing SAS (version 8.0, SAS, Cary, NC) Proc PDIFF at $P \leq 0.05$.

^x non-significant

Table 4. Residue removed from apple leaves from 3 treatments over 5 years in Kearneysville, WV.

	2005	2007	2008	2009	2010	mean
Treatment	g residue/m ² leaf area					
Control	2.8 c ^z	1.3 c	0.4 c	1.5 c	0.6 c	1.32
3% PKPF	3.5 b	2.2 b	1.5 b	2.6 b	1.7 b	2.30
12% PKPF	6.7 a	3.7 a	4.1 a	8.2 a	4.7 a	5.48

Values are the mean of 10 leaves/tree and 3 trees per treatment.

^z Mean values within a column followed by the same letter are not significantly different ($P=0.05$) based on Ryan-Einot-Gabriel-Welsch multiple F test.

Table 5. Effect of treatments on ozone degradation through whole canopy chambers.

Treatment	Ozone (ppb)
air	27 a ^z
Empty chamber	24 b
Untreated control	25 b
0.3% alfalfa	23 c
3% PKPF	23c
2.7% PKPF + 0.3% alfalfa	19 d

Values are the mean of ozone concentration measured from 1000 to 1600 HR over a 10 day period.

^z Mean values within a column followed by the same letter are not significantly different ($P=0.05$) based on Ryan-Einot-Gabriel-Welsch multiple F test.

Table 6. Components of yield and summer pruning weights of ‘Empire’ apple with 4 treatments over 2 years in Kearneysville, WV.

Treatment	Year	Fruit/tree	Summer	
			fruit	pruning fresh
			mass (g/fruit)	weight (kg/tree)
0.3% alfalfa	2011	597 b ^z	133	
3% PKPF	2011	617 b	135	
2.7% PKPF +0.3% alfalfa	2011	651 a	136	
Control	2011	549 c	137	No data
0.3% alfalfa	2012	127	148 a	13.5
3% PKPF	2012	123	138 b	13.3
2.7% PKPF + 0.3% alfalfa	2012	118	144 ab	12.5
Control	2012	139	137 b	13.2 ns.

^z Mean values within a column and year followed by the same letter are not significantly different ($P=0.05$) based on Ryan-Einot-Gabriel-Welsch multiple F test.

Figure 1. The relationship between maximum May ozone levels and May mean temperatures with the increase in fruit mass relative to the irrigated control treatment for 2005-2010 in Kearneysville, WV.

Figure 2. The relationship between calcined kaolin and alfalfa particle density and the degradation of ozone passing over the residue in laboratory studies.

Figure 3. Photosynthetic rates of ‘Empire’ apple trees with 4 treatments over a 10 day period in 2011 and the ambient ozone levels in Kearneysville, WV.

Figure 4. Relationship between the density of extracted leaf residue and the density of DNA contained in the residue for 4 treatments applied to 'Empire' apple in 2011 and 2012.