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Literature Review - Pigments in Plant Health

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Applicability of Pigment Compounds for Improving Plant Health

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Literature Review

Abstract

The solar radiation received at the Earth's surface helps power the photochemical processes in photosynthesis. However, under sunlight, photosynthetic organisms are unavoidably exposed to potentially harmful levels of ultraviolet and visible light radiation. Consequently, plants have developed many mechanisms for the avoidance and dissipation of excess light energy. The growth of crops under increased solar irradiance during sub- and supra-optimal temperature conditions is an obstacle for increasing seasonal crop production in the transition zone. New methods for reducing the photoinhibitory effects of solar irradiation have been observed in the field of turfgrass. Through the application of pigment compounds to the surface of plant leaves, it may be possible to reduce levels of solar incident light exposure to the plant, during temperatures where the fixation of CO_2 is a limiting factor in Photosystem II repair. This proposal will explore the applicability of various commercial and naturally derived pigment compounds for improving the photosynthetic capacity of creeping bentgrass plants under supraoptimal light and sub- and supra-optimal temperature stress.

Creeping Bentgrass

Creeping bentgrass (*Agrostis palustris* ssp. *stolonifera* L.) is a fine textured C3 turfgrass used on golf course greens due to its ability to tolerate low-mowing heights (Warnke, 2003). The aesthetic and performance properties of creeping bentgrass has led to its use in supraoptimal temperature climates, where its health will decline in summer months (Carrow, 1996). For cool-season turfgrasses, ambient air temperatures above 24 C and soil temperatures above 18 C are considered to be supraoptimal for shoot and root growth, respectively (Beard, 1973). Hot and humid conditions in the southeast can produce temperatures above these optimal levels, resulting in a range of symptoms characterized as Summer Bentgrass Decline (SBD) (Carrow, 1996). High air and soil temperatures lead to an increased respiration rate in bentgrass roots, and subsequent dieback upon carbohydrate depletion (Xu and Huang, 2000; Xu & Huang, 2001). In particular, supraoptimal soil temperatures have been shown to be most detrimental to creeping bentgrass root and shoot growth and nutrient uptake (Xu & Huang, 2000). Heat can also disrupt the plant's cellular membranes, severely affecting cellular function (Larkindale & Huang, 2004).

Evaporation and transpiration release heat energy through latent heat of vaporization, which describes the transfer of energy in the state change of water from a liquid to a gas form. Conversely, the same amount of energy is released when water condenses from vapor to liquid form. In other words, evaporation will cool a surface, while condensation will warm it (Tarara, 2000). Differences between water vapor concentration in and outside the plant will determine rates of transpiration. Under conditions of increased humidity, transpirational cooling will decrease, due to reductions in the water vapor concentration gradient between the plant and the air (Rawson, Begg, & Woodward, 1977). However, an increased surface temperature will cause an exponential increase in water vapor concentration at the surface, raising this gradient, which leads to greater transpirational flow of water vapor from the plant.

Consequently, very small changes in temperature can trigger large fluxes in the rate of transpiration (Gates, 1965; Pallardy & Kozlowski, 2008).

Radiation is the largest contributor to increasing soil temperatures (Huang, 2002; Larkindale & Huang, 2004). The root zone of USGA (United States Golf Association) certified golf course greens incorporate high amounts of sand near the surface of the soil (Moore, 2004). Among various soil-types, Abu-Hamdeh & Reeder (2000) observed the highest thermal conductivity in sandy soils. The temperatures of the various soils were positively correlated with bulk density. Research has shown that the addition of organic matter will decrease bulk density (Hummel, 1993). Creeping bentgrass cultivars utilized in golf course greens exhibit high rates of organic matter accumulation at the soil surface (Carrow, 2004; Hudson & Shane, 1994). This accumulation of organic matter will reduce bulk density, and thus thermal conductivity. However, organic matter can also increase water retention, which dramatically increases thermal conductivity with increases in temperature (Abu-Hamdeh & Reeder, 2000; Campbell, Jungbauer, Bidlake, & Hungerford, 1994). Bare portions of the turf will also expose surface organic matter, which will absorb higher amounts of incident light energy due to its darker color (Bristow & Horton, 1996; Loughrin & Kasperbauer, 2003). Heat will either move upward to the surface of soil, or downward from warmer to cooler layers (Tarara, 2000).

Increases in leaf lipid saturation levels have been observed following heat treatment to creeping bentgrass plants (Larkindale & Huang, 2004). The thylakoid membrane contains a large proportion of non-bilayer forming lipids, which are thought to be required for the stabilization of contained Photosystem-II molecules (Thomas et al., 1986). Increases in lipid saturation, within chloroplast structures, allow for a higher tolerance of temperatures, reducing phase-separation of non-bilayer

forming lipids from the chloroplast membrane (Gounaris et al., 1983). However, no changes in lipid composition concentration were observed in the roots of creeping bentgrass (Larkindale & Huang, 2004). Incidences of heat damage have been shown to be light-mediated, supporting the idea that any subsequent damage could occur as a result of light induced damage to the photosynthetic apparatus (Larkindale & Knight, 2002). This idea is supported in creeping bentgrass species, where photosynthetic acclimation has been shown to be essential for increases in tolerance to severe heat stress, due to maintenance of light-harvesting capacity and carbon fixation throughout the heat stress period (Liu & Huang, 2008). The specific mechanisms relating to light induced inhibition of the photosynthetic apparatus will be further discussed later.

Light and Plant Pigments

Visible light (400-700 nm) accounts for 43% of the energy in the global solar irradiance spectrum (300-2500 nm) for North America. The remainder of this energy arrives as 52% near-infrared (NIR) (700-2500) and 5% ultraviolet (UV) (300-400 nm) (Levinson et al., 2005*b*; American Society for Testing and Materials [ASTM], 2003). NIR wavelengths are responsible for much of the heating within leaves (Forbes & Watson, 1992). Consequently, plant leaves will effectively scatter and reflect 70% of incident perpendicular infrared radiation; reducing heat-buildup in the plant and the soil (Knipling, 1970; Atwell, Kriedemann, & Turnbull, 1999; Larcher, 2003). Plants exhibiting bicoloration (abaxial surface a lighter shade of green than adaxial), a thicker cuticle, and a higher portion of mesophyll surface area exposed to intercellular air spaces per unit leaf surface area exhibited predictably higher NIR reflectance values from the adaxial leaf surface. However, in plants with lower pigment content, less incident UV-visible light would be absorbed and less NIR light would be reflected, allowing greater amounts of heat energy to build in the soil, as well as be reradiated as heat. Kopsell, Lefsrud, Sorochan, & McElroy (2010) reported that, among

heat-tolerant cultivars of *Poa pratensis*, those highest in pigment content were the least heat tolerant. However, also mentioned is the possibility that drought was an influencing factor in decreasing pigmentation across cultivars, which would account for a decrease in transpirational cooling and CO_2 fixation. Dry plant leaves will also show diminished reflectance in the NIR, which would increase NIR absorbance by the soil (Hawley, 1971).

Light consists of both wave and particulate properties. While light is propagated in wave form, its interaction with matter is more particulate (Prasad, 1997). Planck's law (Planck, 1989) describes how light exists in quanta, or bundles of energy. This theory was further developed by Einstein (1905), who went on to discover that radiation processes involve the emission or absorption of light quanta, or "photons" (Bohr, 1949). The energy of a photon is determined by its wavelength, the distance between repeating waves, and frequency, the number of light wave repetitions per unit time. Their relationship is considered directly proportional, in that any fraction of photon wavelength equals its reciprocal in energy output, and is a function of frequency (Prasad, 1997). This is not to be confused with the intensity of light, which depends on how many photons of energy are being emitted per unit time (McDonald, 2003).

Two basic principles of light that govern the absorption properties of plant pigments are the Grotthus-Draper and Stark-Einstein laws. The Grotthus-Draper law states that photochemical processes can only occur with absorbed radiation, and the Stark-Einstein law states that each absorbed photon can only affect one molecule (Diffey, 2002). When plant pigment molecules in an unexcited ground state absorb photons of a compatible wavelength, a valance electron is quickly raised to an excited state. After returning to a ground state, the absorbed energy is released in the form of thermal dissipation, fluorescence, phosphorescence, or inductive resonance (McDonald, 2003). However, long-term exposure

of plants to supraoptimal levels of light can result in the photodestruction of photosynthetic pigments. This chemical reaction is considered oxygen- and light-dependant, and is defined as photooxidation (Powles, 1984). Light toxicity occurs when high flux light converts the target pigment molecules into an excited state, first, an initial short-lived singlet state, followed by molecular rearrangement into a longer-lived triplet state. During this time, there is an increased chance for chemical reactions with surrounding molecules. In the formation of damaging species, triplet energy is transferred to molecular oxygen, forming singlet oxygen. This reactive oxygen species exists as a free radical, capable of oxidizing and bleaching plant pigments to an irreversible degree under extreme conditions (Larson, 1988). However, plants have evolved multiple protective mechanisms for the effective removal of this excess light energy.

Photosynthetic systems are composed of a network of principal and accessory pigments (Duysens & Amesz, 1962). While principal pigments are directly involved in the chemical conversion of energy, accessory pigments act as sinks for conducting different wavelengths, transferring the energy to the primary through inductive resonance. Together, these pigments form a network of overlapping absorption bands, improving the efficiency at which plants harvest light in the action spectrum of photosynthesis (Smith & French, 1963; McCree, 1971). However, accessory pigments also play an important role in photoprotection.

Functioning as an accessory pigment, carotenoids of the xanthophyll cycle are considered essential to the dissipation of energy under conditions of excess light, through the interception and removal of excess excitation energy prior to its entrance into the electron transport chain (Demmig-Adams & Adams III, 1996). Once the absorption of light exceeds a plant's capacity for CO_2 fixation, photosynthetic electron transport generates a decrease in lumen pH. This activates the conversion of xanthophylls, removing oxygen from violaxanthin

to form antheraxanthin, then zeaxanthin, which dissipates the excess energy as heat (Muller, 2001).

Flavanoids, another group of accessory pigments, make up one of the largest known groups of phenolic compounds within plants, with over 9000 assessed from plant tissue as reported by Williams & Grayer (2004). Responsible for the many bright blue, red, and purple colors throughout nature, anthocyanins are the most widespread of the pigmented flavonoids (McDonald, 2003). The prospective roles of anthocyanin in plants are numerous, and have been contemplated by scientists for well over a century (Gould, 2010). As stated by Wheldale (1916), in one of the earliest reviews of plant anthocyanin function, "It is difficult to find a hypothesis which fits all cases of anthocyanin distribution without reduction to absurdity." However, in recent years there have been many significant advances in understanding the roles of anthocyanin pigments in plants. Related to its light-attenuation properties, anthocyanin accumulation has been linked to photoprotection of chlorophyll during drought and cold stress (E. Taulavuori, Tahkokorpi, Laine, & K. Taulavuori 2010, Gould, Dudle, & Neufeld, 2010), improved recovery from mechanical injury (Gould, McKelvie, & Markham, 2002), enhanced nutrient retrieval from senescing leaves (Hoch, Singsaas, & McCown, 2003), and delayed senescence in CO_2 rich environments (Tallis, Lin, Rogers, Zhang, Street, Miglietta, Karnosky, De Angelis, Calfapietra, & Taylor, 2010). Independent of its light attenuation properties, anthocyanin has also been ascribed to many biotic-dependant roles, including: microbial defence responses (Kangatharalingam, Pierce, Bayles, & Essenberg, 2002; Hipskind, Wood, & Nicholson, 1996); herbivory avoidance (Karageorgou & Manetas, 2006); and pollination ecology (Harborne & Smith, 1978). Due to the diverse range of inducing factors associated with anthocyanin biosynthesis, correlating the transient

accumulation of anthocyanin to any one function is inherently difficult. Consequently, knowledge of the localization and spectroscopic properties *in vivo* of all the pigment pools is essential for ecophysiological studies and the quantitative description of anthocyanin function (Gould et al., 2002). While its distribution in plants differs considerably across species, anthocyanin will generally localize within cell vacuoles, in or just below the adaxial epidermis, effectively providing light-protection to subjacent chloroplasts (Merzlyak, Melo, & Naqvi, 2008). Abaxial accumulation in leaves has been observed, but is also considered a photoprotective adaptation of light-sensitive plants whose leaf orientation and substrate albedo may vary throughout developmental stages of the plant (Hughes & Smith, 2007).

Anthocyanin's ability to protect plant tissue during events like wounding, drought, and pathogen infection can also be considered an indirect effect of light screening, due to an avoidance of light-dependant oxidation of tissue through reductions in excitation pressure during periods of increased tissue vulnerability (Steyn, Wand, Holcroft, & Jacobs, 2002). In light of this observed reduction in the accumulation of reactive oxygen species, there has been an inescapable interest in the potential role of flavanoids as antioxidants *in vivo*. A study by Rice-Evans, Miller, & Paganga (1997), demonstrated the *in vitro* antioxidant capacity of plant-derived flavonoids to be several times more effective than both ascorbate (vitamin C) and α-tocopherol (vitamin E), two functional antioxidants in plants. This would suggest potential antioxidant benefits associated with flavonoid presence *in vivo*. However, the chemical diversity and complex biochemistry of flavonoids *in vivo* have prevented adequate correlations between flavonoid accumulation, flavonoid oxidation products, and oxidative stress. Consequently, the putative function of flavonoids as antioxidants is still a matter of debate (Hernández, Alegre, Van Breusegem, & Munné-Bosch, 2009).

New Models of Photoinhibition

Photosynthesis requires the interaction between two separate, but equally complex photosystems. Photosystem I (PSI) and Photosystem II (PSII) have designations of P700 and P680 respectively, named for the absorption maximum of their chlorophyll *a* molecules. Each of the photosystems contains subtle differences in protein associations, which accounts for their different absorption properties (Anderson & Andersson, 1988). Chlorophyll *a* molecules only absorb a small portion of light for use in photosynthesis. In order to better utilize the reaction centres in photosynthesis, each photosystem utilizes antenna complexes composed of several hundred pigment molecules. These light-harvesting complexes help to extend the absorption spectrum, using resonance transfer to designate the flow of excitation energy to the reaction centres (Glazer, 1989; Hunter, van Grondelle, & Olsen 1989; Zuber, 1986).

The absorption of excess light energy has the potential to damage photosynthetic machinery, beginning with PSII. Photoinactivation of PSII is hypothesized to occur by two separate mechanisms, acceptor-side and donor-side, which both result in the inhibition of electron transfer in PSII, and subsequent degradation of the D1 protein (Wei, Cady, Brudvig, & Hou, 2011). PSII reaction centre D1 proteins, which exhibit the highest turnover rates in the thylakoid membrane, are the main target of oxidation during photodamage (Sunby, McCaffery, & Anderson, 1993). In the acceptor-side mechanism hypothesis, photoinhibition begins with the reduction of the plastquinone pool under intense light, causing a lack of oxidized plastoquinone to bind to the Q_B site on the D1 protein. Because Q_A^- is unable to transfer an electron to Q_B, it becomes doubly reduced to Q_A^{2-} during the second turnover of the reaction centre. In order to become stable, Q_A^{2-} will become protonated, forming Q_AH_2, which is then released from the Q_A binding site on the D1 protein. The newly unoccupied Q_A site leads to the formation of the primary radical pair $P680^+Pheo^-$, and through recombination, generates triplet state P680. This reacts with oxygen to form singlet oxygen, a

reactive oxygen species responsible for D1 protein degradation (Wei et al., 2011; Tyystjärvi, 2008; Anderson, Park, & Chow, 1998). In the donor-side mechanism hypothesis, highly reactive $P680^+$ is formed due to a lack of electron donation while under the influence of light. $P680^+$ will oxidize surrounding chlorophyll and carotenoid molecules, and lead to degradation the D1 protein (Wei et al., 2011).

Under experimental light conditions, photodamage to PSII was found to be greatest in regions of UV and yellow light exposure in *Arabidopsis thaliana* (Takahashi, Milward, Yamori, Evans, Hillier, & Badger, 2010). Damage to PSII by high energy light can best be explained by a new two-step model developed by Ohnishi, Allakhverdiev, Takahashi, Higashi, Watanabe, Nishiyama, & Murata, (2005) and further explained by Tyystjärvi (2008). This theoretical model states that photoinhibition begins with the reduction of the Mn cluster in the oxygen-evolving complex by UV, blue, and green light, but not red (Wei et al., 2011). Following Mn inactivation, PSII becomes sensitive to light at 680 nm, experiencing inactivation from direct red and blue light exposure to its photosynthetic pigments in the donor-side mechanism (Ohnishi et al., 2005). Damage to the oxygen-evolving complex will increase potential for PSII damage due to reductions in electron donation from the oxygen evolving complex to PSII undergoing oxidation (Hakala, Tuominen, Keränen, T. Tyystjärvi, E. Tyystjärvi, 2005). Takahashi et al. (2010) attempts to explain the adverse effects of yellow light, attributing its photoinhibitory effects to the manganese light-sensitizer mechanism. While yellow light contains less excitation energy than ultraviolet (UV) and blue light, it is much more abundant in the solar spectrum (Takahashi & Badger, 2010). More of this light is able to penetrate plant tissue, due to its lack of absorption by anthocyanin (primarily blue and green light absorption), chlorophyll (primarily blue and red light absorption) and carotenoid (primarily blue and green light absorption) pigments (Takahashi et al., 2010; Solovchenko & Merzlyak, 2008). The PSII photodamage spectrum is very different from the absorption

spectra of these pigments, but is closely correlated with that of manganese compounds (Wei et al., 2011). Because collimated light is scattered within leaf tissue, the efficiency of its absorption will increase with depth in the mesophyll (Vogelman, Nishio, & Smith, 1996). This allows non-photosynthetic yellow and green light to penetrate more deeply into the leaf, and trigger excitation in shade adapted chloroplasts of the lower mesophyll (Nishio, 2000). The increased presence of refracted yellow-green light in the mesophyll may have a greater influence on Mn excitation in the absence of high energy UV light. This suggests that the mechanism of light diffusion, meant to increase the absorption of light by pigment networks, could also contribute to the indirect photodamage of PSII during high visible light irradiance (Takahasi et al., 2010). However, a recent study revealed that visible light had little impact on the production of high valent species of Mn in the oxygen evolving complex, while UV light did (Wei et al., 2011). Consequently, UV light inhibition of the oxygen evolving complex in PSII is also much faster and thus more damaging than that of visible light (Tyystjärvi, 2008). Wei et al. (2011) uses this to support the idea that excess visible light induced photodamage occurs directly to PSII, without inhibiting the Mn oxygen-evolving complex. This supports the theory that, while donor-side photoinhibition has often been observed after chemical inactivation of the oxygen evolving complex by UV light, there is still potential for visible light to trigger this mechanism in the absence of UV and blue light, because the OEC will sometimes fail to reduce highly reactive $P680^+$ species (Anderson et al., 1998; Wei et al., 2011). The absorption peak of anthocyanin in the visible light region (450-550 nm), suggests that it may provide photoprotection in this mechanism as well (Solovchenko & Merzlyak, 2008). Overall, the close correlation between this photodamage spectrum and the anthocyanin absorbance spectrum supports the

hypothesis that adaxial localized phenolic coumpounds are meant to act as filters for high

energy light (Takahashi & Badger, 2010).

PSII Repair Cycle

Upon photodamage to PSII, the plant begins to replace damaged PSII proteins in a

process known as the PSII repair cycle (Aro, Suorsa, Rokka, Allahverdiyeva, Paakkarinen,

Saleem, Battchikova, & Rintamäki, 2004). In order to repair the damaged PSII complex, the

photodamaged D1 protein is rapidly degraded, *de novo* synthesized, and incorporated back

into PSII (van Wijk, Roobol-Boza, Kettunen, Anderson, & Aros, 1997; Nishiyama,

Yamamoto, Allakhverdiev, Inaba, Yokota, & Murata, 2001). Environmental stresses can

inhibit *de novo* synthesis of the D1 protein, and consequently limit the rate and extent of PSII

repair (Allakhverdiev & Murata, 2004). In forming a common mechanism for this inhibitory

response, the role of reactive oxygen species seems likely. The fixation of CO_2 is sensitive to

a wide array of environmental stresses: including light (Sun, Nishio, & Vogelmann, 1996),

temperature, drought (Cornic & Ghashghaie, 1991) and salt (Yeo, Caporn, & Flowers, 1985).

Limitation of CO_2 fixation decreases NADPH use efficiency, subsequently reducing $NADP^+$,

a major acceptor of electrons in PSI. This accelerates the rate of electron transport to

molecular oxygen, forming superoxide anions, which lead to formation of H_2O_2 by

superoxide dismutase in PSI (Takahashi & Murata, 2008). The reaction for scavenging of

H_2O_2 is the photoreduction of dioxygen to water in PSI by the electrons derived from water in

PSII. The increased production of H_2O_2 can exceed the rate at which it can be scavenged in

the water-water cycle (Takahashi & Murata, 2008; Asada, 1999; DeRose, Mukerji, Latimer,

Yachandra, Sauer, & Klein, 1994; Barber, 2008; Song, Liu, Wang, Li, & Liu, 2006).

Unscavenged H_2O_2 inhibits the repair of PSII through blocking the synthesis of a D1

precursor (Apel & Heribert, 2004; Nishiyama et al., 2001). Though these reactions have no

effect on the rate of photodamage to PSII, with repair inhibited, photoinhibition is accelerated due to on-going damage incurred from light exposure (Takahashi & Murata, 2005).

Adaxial localized screening pigments increase the reflectance of red light, the absorbance of blue light, and the attenuation of green light. In an effort to better understand the role of adaxially localized pigment compounds in preventing photoinhibition in the lower mesophyll, Hormaetxe, Becerril, Fleck, Pintó, & Garcia-Plazaola (2005) tested the filtration qualities of variously colored cultivars of *Buxus sempervirens* when under photoinhibitory conditions. Adaxial sections of green, brown, orange yellow, and red colored cultivars were positioned *in loco* of adaxial removed sections of green shade leaves. Green adaxial sections demonstrated the highest levels of absorptance, and consequently, the lowest levels of photinhibition in the lower mesophyll. These results are most likely due to the increased light absorption efficiency and photostability of high chlorophyll content leaves, whereas the accumulation of light filtration pigments is usually associated with lower levels of chlorophyll, and thus lower light use efficiency (Close & Beadle, 2003). Assuming this higher light protection by chlorophyll in the adaxial section of the leaves of this species, researchers should begin to ask why certain plants didn't evolve specialized green pigments for the more effective filtration of excess light (Hormaetxe et al., 2005).

Commercial Pigments

Over recent years there has been an increasing interest in the utilization of "stress guard" pigments in the field of turfgrass science. In 2004, a patent was filed for the commercial use of Pigment Green 7, a polychlorinated form of copper phthalocyanine, on turfgrass plants. Under supraoptimal heat stress, creeping bentgrass plants treated with copper

phthalocyanine showed increases in quality, chlorophyll content, carotenoid content, and photochemical efficiency when compared to controls.

Copper phthalocyanine; specifically Pigment Green 7 (chlorinated copper phthalocyanine), has a long history of application across many industries. It has mainly seen use in outdoor paints, due to its increased dispersibility, light fastness, heat stability and durability (Kadish, Smith, & Guilard, 2003; Tracton, 2006). More recently, it has begun to see use as a photosensitizer in dye-sensitized organic solar cells (Huang, Yu, Lin, & Jiang, 2009; Chu, Shrotriya, Li, & Yang, 2006; Tripathi, Datta, Samal, Awasthi, & Kumar, 2008). This use can be attributed to the structural and spectroscopic similarities of copper phthalocyanine to plant chlorophyll compounds (Ludwig, Strohmaier, Peterson, Gompf, & Eisenmenger, 1994; Karan, Basak, & Mallik, 2007; Bohn & Walczyk, 2004). Naturally, this has resulted in many experiments evaluating their efficiency in harvesting solar energy (Farag, 2007).

Copper pthalocyanine (pthalocyanine blue) and chlorinated copper phthalocyanine (phthalocyanine green) are pigments known for their excellent light and heat stability, allowing them to maintain structure under outdoor conditions. In general, all copper phthalocyanines are considered weakly scattering pigments, with strong absorption in the red to near-infrared (NIR) portions between 500 to 700 nm, the UV region between 300 and 400 nm and equally strong fluorescence in the UV-blue between 350 to 500 nm. Its UV-blue absorption and fluorescence spectrum strongly overlap the emission band of UV light capable of high photoinhibition efficiency in the excitation of manganese in the oxygen evolving complex between 300 and 500 nm (Levinson, Berdahl, & Akbart, 2005*a*; Levinson, Berdahl, & Akbari, 2005*b*; Bigger & Delatycki, 1989; Saron, Zulli, Giordano, & Felisberti, 2006; Hakala et al., 2005). Plants are only able to reflect very small amounts of UV radiation (~3%) (Larcher, 2003). Copper phthalocyanine's ability to attenuate extremely high levels of

incident high energy light with minimal scattering, may allow it to effectively reduce levels of bentgrass photoinhibition. By adjusting the density at which the pigment is applied via a carrier (i.e. – water), the level of incident light attenuation can be adjusted to meet the high-light avoidance needs of the plant. The largest dip in light attenuation by copper phthalocyanine occurs at 550 nm, allowing it to closely mimic the action spectrum of photosynthesis, and have a green color (McDonald, 2003; Saron et al., 2006).

Pigments more capable of reflecting NIR light have been shown to be much cooler in sunlight that those that absorb NIR. This has been shown to have particular importance in roofing, where the use of roofs with NIR reflecting pigments has been shown to significantly reduce building heat gain over that of roofs utilizing NIR absorbing pigments (Levinson et al., 2005*a*; Levinson et al., 2005*b*). This has led to the identification of dark colored pigments that have the ability to reflect infrared heat-building rays to the same degree that a white roof would (Miller, Akbari, & Levinson, 2004).

In the Norton et al. (2006) patent for utilizing copper phthalocyanine to improve turfgrass quality, there was specific interest on the increased efficacy of phthalocyanine green pigments over that of phthalocyanine blue. Spectroscopically, the largest difference between phthalocyanine blue and phthalocyanine green is that phthalocyanine green absorbs more strongly in the 700-1000 nm region, which contains half of the NIR solar energy and a quarter of the total solar energy received by North America (Levinson et al., 2005*a*; Levinson et al., 2005*b*). This would indicate that phthalocyanine green's efficacy over phthalocyanine blue is related to an increase in NIR absorbance, and a potentially greater build-up of heat.

In materials science, interfacial heat transfer is characterized by thermal boundary resistance, which causes a temperature discontinuity at the interface of two materials. This is important, as the efficiency of thermal transport across dissimilar interfaces (i.e.-copper pthalocyanine/plant) will determine levels of heat dissipation (Jin, Yadav, K. Sun, H. Sun, Pipe, & Shtein, 2011). Jin et al. (2011) recently discovered a low thermal conductivity between copper phthalocyanine and metal, indicating the presence of a large thermal boundary resistance. Plant leaves naturally have lower thermal conductivity than metals (Dixon & Grace, 1983).

Phthalocyanine blue and phthalocyanine green are both insoluble, taking the appearance of powders. The weak scattering properties of theses copper phthalocyanines are due to their small particle size, which is typically 120 nm in diameter (Levinson et al., 2005*b*). Chlorophyll is also water-insoluble; however chlorophyll *a* and *b* molecules are much smaller at less than 2 nm in diameter (Yu, Yang, & Kim 2010; Cofrancesco, 2000; Strebeyko, 2000).

Chlorella, a unicellular green algae, was first recognized through isolation by Beijernick (1890). Among known photosynthetic organisms, it is highest in chlorophyll production, capable of performing photosynthesis at a rate much higher than that of many plant species. Its biomass also contains high concentrations of carotenoid pigments that are capable of providing unique health benefits in humans (Cha, Koo, & Lee, 2008). Since their introduction to the health market during the 1960s, *Chlorella* species have experienced a pronounced growth in production for use as health supplements. One of the most popular species for these applications is *Chlorella vulgaris* (Kanno, 2005). Capable of being cultivated in large scale bioreactors, *Chlorella vulgaris* holds a significant advantage over that of higher plant species, providing a cheap and reliable source for the mass production of beneficial nutrients (Scragg, Illman, Carden, & Shales, 2002).

Ranging from 2 to 10 μm in diameter, *Chlorella vulgaris* cells have a globular shape, and a strengthened cell wall that prevents its adequate digestion and beneficial uptake in humans. For this reason, its cells are fragmented following cultivation, allowing its cell contents, particularly lutein, to have greater bioavailability in humans (Mitsuda, Nishikawa, Higuchi, Nakajima, & Kawai, 1977; Shibata & Hayakawa, 2009). Commercially available forms of *Chlorella vulgaris* thus consist of fragmented cells sold as a powder (Görs, Schumann, Hepperle, & Karsten, 2010).

The absorption spectrum of *Chlorella vulgaris* has light attenuation properties similar to that of chlorinated copper phthalocyanine, with peaks in the NIR region at 600 to 700 nm and the UV-blue light region at 400-500nm (Ley & Mauzerall, 1982; Yun & Park, 2001). It is hypothesized that the foliar application of pulverized Chlorella vulgaris cells can improve creeping bentgrass health under suproptimal levels of light exposure.

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