Advanced Oxidation to Eliminate Growth Inhibition and to Degrade Plant Protection Products in a Recirculating Nutrient Solution in Rose Cultivation

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Abstract

The EU Water Framework Directive demands a sound ecological and chemical basis for ground and surface waters. This has motivated the Dutch greenhouse industry to seek more sustainable water management procedures which will enable a zero-emission of nutrients and plant protection products (PPP) in the year 2027. Although closed soilless growing systems are widely applied in The Netherlands, it appears that discharge of nutrients varies between 5 and 40%. Discharge based on salinity is only a minor part, up to 15%. In rose cultivation, growth inhibition is the major reason for discharge of the nutrient solution. Former research could not find a proper reason for growth inhibition, but it is most likely of organic origin. The water treatment method of advanced oxidation, at which first hydrogen peroxide is added, directly followed by an exposure to UV-C light (200-280 nm), is known to degrade large organic molecules. Therefore this method has been investigated to eliminate growth inhibition and also to degrade PPPs. Among all methods advanced oxidation has been a first choice because many rose growers already possess a UV installation for elimination of pathogens from the recirculating solution. Trials with advanced oxidation have been performed at two rose nurseries at which the dosages of hydrogen peroxide (0-25 mg/L) and UV lighting (0-900 mJ/cm^2) have been varied to search for indications for elimination of growth inhibition and the degradation of PPPs. After treatment samples were taken to test for growth inhibition of the solution in a bioassay, Phytotoxkit; the chemical composition; the residual amount of PPPs and the presence of micro-organisms. Preliminary results show that (1) growth inhibition exists and can be decreased, (2) plant protection products can be degraded, (3) pathogens have been eliminated and (4) composition of the nutrient solution is unchanged except for iron.

INTRODUCTION

The European Water Framework Directive (WFD, 2000) demands a "good status" for surface and groundwater to be achieved by 2015. If the goal cannot be achieved in time additionally two 6 year periods of phasing may be used. The Dutch greenhouse industry, organized within the covenant "Greenhouse and Environment" between employers and government, agreed to come to an almost zero emission of nutrients and plant protection products (PPP) by 2027. A first step to be taken is the reduction of the discharge of the used nutrient solution in soilless cultivation systems. During the cultivation of roses the level of discharge was higher (15-40% of the amount of water supplied) compared to other crops (5-10% of the amount of water supplied). One reason is the susceptibility of rose to high sodium levels and associated EC (Baas and Van den Berg, 1999; De Kreij and Van den Berg, 1994). Another reason is the supposed growth inhibition, indicated by an increase in production and/or quality of the produce after discharge of the nutrient solution. The real cause is unknown, but the phenomenon has been reported by several authors (Ehret et al., 2005; Pramanik et al., 2000; Jung, 2003; Van Os et al., 2004). Up to now it is unclear if growth inhibition is caused by root

exudates, accumulation of plant protection products, microbial reactions, other reasons or a mixture of these. In The Netherlands rose growers claim an ability to forecast that growth inhibition is about to appear and start to discharge used nutrient solution. From frequent analyzing the drain water it is clear that there is no inorganic cause (EC, pH, sodium contents, unbalanced nutrient solution); consequently there may be an organic cause in the nutrient solution.

The degradation of PPPs, large organic molecules, in water can be achieved with advanced oxidation (Pickhardt, 2007; De Jong et al., 2005; Stasinakis, 2008; Badawy et al., 2006; Kruithof et al., 2003, 2007), which is in use to purify industrial or household wastewater and for drinking water preparation. One form of advanced oxidation is the application of hydrogen peroxide (H_2O_2) immediately followed by a dose of UV-C light (200-280 nm). As growers often have a UV installation for eliminating pathogens from the nutrient solution (Van Os, 2009) additional hydrogen peroxide dosing equipment is applicable at relatively low cost.

In the present research project (Van der Maas et al., 2010) there is no focus on finding individual substance(s) responsible for growth inhibition. The goal is to prevent growth inhibition by breaking down large, organic molecules. A second goal is to demonstrate the degradation of PPPs to such a level that discharge to surface water is of no harm to the environment (below maximum accessible risk level, MTR). The final objective for the growers should be to recirculate as long as possible and only discharge (part of) the used nutrient solution because of an unbalanced solution or excessive levels of sodium or other salts.

MATERIALS AND METHODS

An experimental set-up was made to test the advanced oxidation method for the elimination of growth inhibition and for the degradation of PPPs. Firstly, comparison was made between nurseries to investigate the presence of growth inhibition. A difference in growth inhibition between cultivars was found. An appropriate company was chosen (presence of HP-UV installation, sensitive cultivar) and a hydrogen peroxide dosing equipment installed. The UV-C installation is a commercial Priva Vialux disinfection equipment with one high pressure UV-C lamp and tools to control pH, flow and UV intensity to produce a constant preset value for UV dose. H_2O_2 was dosed with a pump into the supply side of the Vialux installation. The effect of advanced oxidation was tested on November 27, 2008 and January 25, 2009 to test the effects on growth inhibition, degradation of PPPs, nutrients and micro-flora (Table 1). On April 7 and May 17 2010 additional measurements (Table 1) were undertaken at another rose nursery as part of a prolonged field test to show the long term effects of full recirculation and treatment with H_2O_2 and HP-UV on yield and quality of roses (to be reported later). UV equipment was similar and H_2O_2 dosing was improved by suction through a calibrated venture system, which doses proportional to the varying flow of the drain water.

To investigate growth inhibition in the drainwater of a rose crop, the Phytotoxkit (Blok et al., 2008, 2007) was selected. Phytotoxkit is preferred above a test with Chinese cabbage and rose cuttings because of clear results, replicability, short term results and lower labour and financial input (results not shown). In November 2008, January 2009, April 2010 and May 2010 respectively 9, 9, 11 and 9 samples were analysed (Table 1). Selected samples of all treatments (respectively 13, 15, 16, 16; Table 1) were sent to several commercial and certificated laboratories to be analysed with mass spectrometry equipment on PPPs, main and spore elements, pH and EC and micro-organisms.

RESULTS AND DISCUSSION

Growth Inhibition

First comparison of Phytotoxkit tests between nurseries showed that growth inhibition depends on the cultivar (results not shown). The November and January trial results at a nursery with a sensible cultivar are presented in Figure 1. Here, advanced

oxidation treatments were compared with the reference (drainwater; 0 UV, 0 H_2O_2) for the relative root length of garden cress. The Phytotoxkit test results of the April and May 2010 trials are presented in Figure 2. These results suggest for the first time that growth inhibition exists and can be eliminated. Due to a limited number of tests (maximum capacity per day to process samples) no statistical analysis is possible and no recipe can be given to eliminate growth inhibition. Further investigations have to show if results for garden cress are similar to rose and which dose is needed. A prolonged field test (in progress) may confirm the correlation between growth inhibition and the Phytotoxkit test. After that a "recipe" may be given to apply advanced oxidation in rose cultivation to avoid or to eliminate growth inhibition.

Degradation of Plant Protection Products

The analyses of Nov. 2008, Jan. 2009, April 2010 and May 2010 on PPP show that some PPPs were degraded with increasing H_2O_2 dosage, some with increasing UV-C dosage, while most were degraded best by a combination of the two. On average, the number of PPPs decreased from 9-14 in the drainwater (before treatment) to 6-10 after treatment at the higher doses. Only a few PPPs decreased for 100%, the other PPPs decreased in concentration between 60 and 100% of the level in the drain water before treatment. About 1-6 PPPs are present above the MTR-level level for surface water. Although treatments cause a degradation of these PPPs, they do not reach this MTR- level in one step (i.e. imidacloprid, cyprodinil, spiroxamine, kresoxim-methyl). Degradation of imidacloprid and cyprodinil is presented in Figure 3 as example for all substances. Imidacloprid is mainly degraded by UV and additionally with H_2O_2, while cyprodinil is mainly degraded by an increasing dosage of H_2O_2. Further statistical analysis will take place on joint 2010 data and additional sampling with even higher dosages of H_2O_2 and UV-C. Preliminary results of additional sampling show that by increasing the dosage to either 50 mg/L H_2O_2 or 1000 mJ/cm2 UV light, degradation of PPPs below the MTR is possible.

Nutrients and Other Parameters

Full nutrient analysis of all treatments has been made. There are no substantial differences between treatments for all elements except for iron (Fig. 4A). Iron chelate degradation is proportional with dose of UV-C light. There is a clear build-up of nitrite (NO_2) at higher dosages of UV-C light. At the same time there is a slight decrease in concentration at increased H_2O_2 dosages (Fig. 4B). Nitrite levels (up to 2.5 mg/L) are well below the presumed crop damage level (10 mg/L) (Voogt, pers. commun.). Oxygen concentration, pH and EC are very stable, while turbidity decreased and transmission slightly increased (larger molecules are broken down in small ones and CO_2) because of higher dosages of H_2O_2 and UV-C and degradation of chemical contents (i.e. iron chelate). Micro-organisms are all eliminated: no pathogens have been detected after treatment.

CONCLUSIONS

The advanced oxidation (H_2O_2 followed by UV-C light) trials with the bioassay Phytotoxkit indicate a correlation between relatively easily obtainable test results and growth inhibition in rose cultivation. The use of advanced oxidation shows that growth inhibition exists and can be decreased and, consequently, that advanced oxidation may become an additional method to extend the recirculation of drain water and thus decrease the discharge of nutrient solution to surface water. Higher dosages of H_2O_2 and UV-C light can degrade a substantial number of plant protection products in the recirculating nutrient solution with 60-100% compared to non-treated drain water. Use of advanced oxidation does not affect the nutrient solution, except for the availability of iron. Further research will lead to more precise recipes for growers to use advanced oxidation either to eliminate growth inhibition and/or to degrade plant protection products. Effects in other cultures may also be investigated.

ACKNOWLEDGEMENTS

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Literature Cited

Baas, R. and Van Den Berg, D. 1999. Sodium accumulation and nutrient discharge in recirculation systems: a case study with roses. Acta Hort. 507:157-164.

Badawy, M.I., Ghaly, M.Y. and Gad-Allah, T.A. 2006. Advanced oxidation processes for the removal of organophosphorus pesticides from wastewater. Desalination 194:166-175.

Blok, C., Persoone, G. and Wever, G. 2008. A Practical and Low Cost Microbiotest to Assess the Phytotoxic Potential of Growing Media and Soil. Acta Hort. 779:367-374.

Blok, C., Aguilera, M. and Van Os, E.A. 2007. Validation of a New Phytotoxicity Test (Phytotoxkit) against an Established Four-Week Growing Test with Pre-Grown Plant Plugs. Acta Hort. 819:209-214.

De Jong, P., Kramer, J.F., Slotema, W.F. and Third, K.A. 2005. Verkenningen zuiverings-technieken en KRW. Stowa report 28, 115p (in Dutch).

De Kreij, C. and Van Den Berg, Th.J.M. 1990. Nutrient uptake, production and quality of Rosa hybrida in rockwool as affected by electrical conductivity of the nutrient solution. p.519-523. In: M.L. Van Beusichem (ed.), Plant Nutrition – Physiology and Applications. Kluwer Academic Publishers, Dordrecht, The Netherlands.

Ehret, D.L., Menzies, J.G. and Helmer, T. 2005. Production and quality of greenhouse roses in recirculating nutrient systems. Scientia Horticulturae 106:103-113.

Jung, M.C.V. 2003. The role of selected plant and microbial metabolites in the nutrient solution of closed growing systems in greenhouses. Ph.D. Thesis, Swedish University of Agricultural Sciences, Agraria 418.

Kruithof, J.C., Kamp, P.C. and Martijn, B.J. 2007. UV/H_2O_2 treatment: a practical solution for organic contaminant control and primary disinfection. Ozone: Science and Engineering 29:273-280.

Kruithof, J.C., Kamp, P.C., Lute, N.W., Belosevic, M. and Williams, G. 2003. Implementation of UV/H_2O_2 treatment for inactivation of micro-organisms and pesticide control, 2nd Int. Congress on Ultraviolet Technologies, Vienna, Austria.

Pickhard, P.W. 2007. Design of a closed water system for the greenhouse horticulture MSc Thesis, Technical University Delft, LTG6-3-1, 112p.

Pramanik, M.H.R., Nagai, M., Asao, T. and Matsui, Y. 2000. Effects of temperature and photoperiod on phytotoxic root exudates of cucumber (*Cucumis sativus*) in hydro-ponic culture. J. Chemical Ecology 26:1953-1967.

Stasinakis, A.S. 2008. Use of selected advanced oxidation processes (AOPs) for wastewater treatment - a mini review. Global NEST Journal 10(3):376-385.

Van der Maas, A.A., Van Os, E.A., Blok, C., Meijer, R.J.M. and Enthoven, N. 2010. Zuivering recirculatiewater in de rozenteelt, fase 0, fase 1, fase 2. Wageningen UR, report GTB-1010, 30p (in Dutch).

Van Os, E.A., Postma, J., Pettitt, T.R. and Wohanka, W. 2004. Microbial optimisation in soilless cultivation: a replacement for methyl bromide. Acta Hort. 635:47-58.

Van Os, E.A. 2009. Comparison of some chemical and non-chemical treatments to disinfect a recirculating nutrient solution. Acta Hort. 843:229-234.

WFD. 2000. EU Water Framework Directive, Water Framework Directive 2000/60/EC. http://ec.europa.eu/environment/water/water-framework/index_en.html

Tables

Table 1. Dosage of H_2O_2 and UV-C in various treatments of advanced oxidation, at which p is sampling for Phytotoxkit, PPPs, nutrients and micro-organisms and x is sampling for PPPs, nutrients and micro-organisms and -- means no sampling.

H2O2 (mg/l)	UV mJ/cm2)	Date Nov. 2008	Jan. 2009	Apr. 2010	May 2010
0	0	p	p	p	p
0	100	x	--	p	p
0	250	x	p	x	x
0	500	p	--	x	x
0	1000	p	--	--	--
5	0	--	x	x	x
5	100	p	--	p	p
5	250	p	p	p	p
5	500	--	p	p	p
5	800	x	--	--	--
10	0	p	p	--	--
10	250	p	p	--	--
10	750	p	x	--	--
10	500	x	p	--	--
15	0	--	x	p	p
15	100	--	--	p	x
15	250	--	p	p	p
15	500	--	p	p	p
15	750	--	x	--	--
25	0	--	--	x	x
25	100	--	--	p	p
25	250	--	x	p	x
25	500	p	x	x	x
		13(9)	15(9)	16(11)	16(9)

Figures

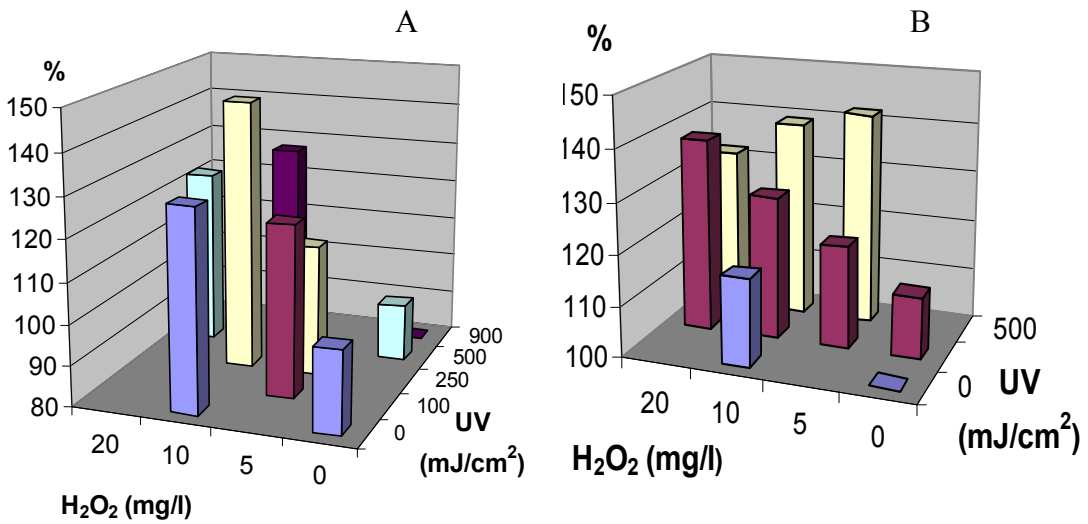

Fig. 1. Effect of advanced oxidation treatments on root length of garden cress as affected by increasing dosage of H_2O_2 and/or UV-C. Left: 27 Nov. 2008. Right: 28 Jan. 2009.

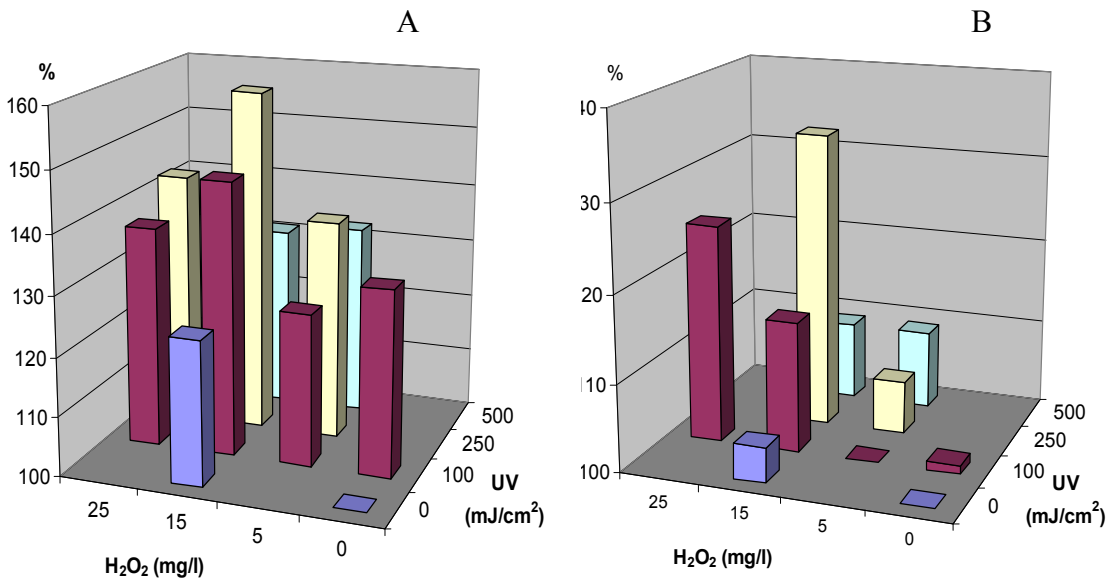

Fig. 2. Effect of advanced oxidation treatments on root length of garden cress as affected by increasing dosage of H_2O_2 and/or UV-C and compared with drainwater (no dosage). Left: 7 April 2010. Right: 17 May 2010.

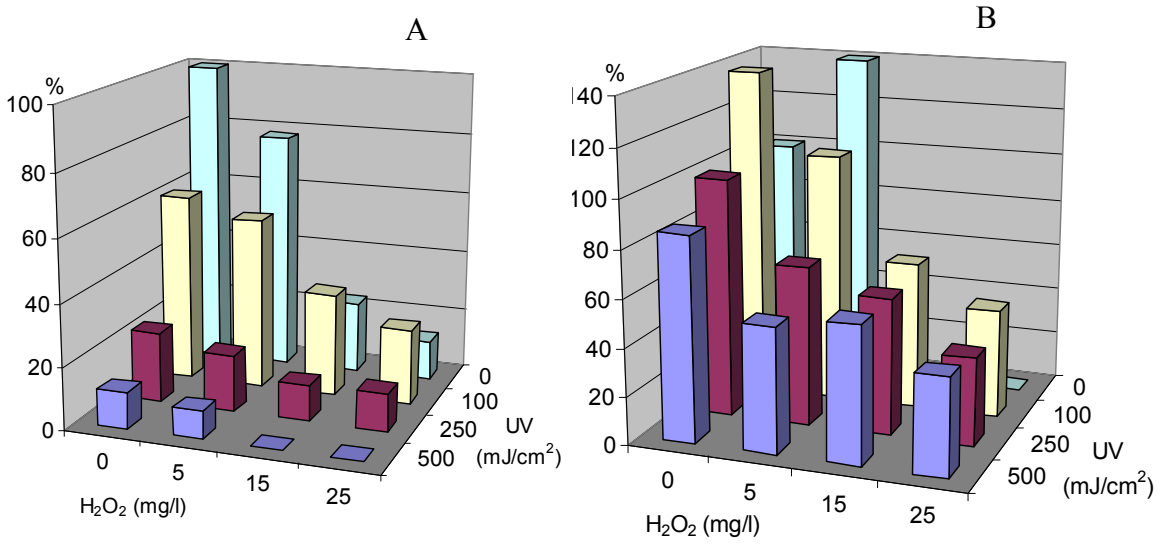

Fig. 3. Degradation of imidacloprid (left, May 17 2010) and cyprodinil (right, April 7 2010) caused by various dosages of H_2O_2 and UV-C compared to drainwater (100%, 0 UV-C and 0 H_2O_2).

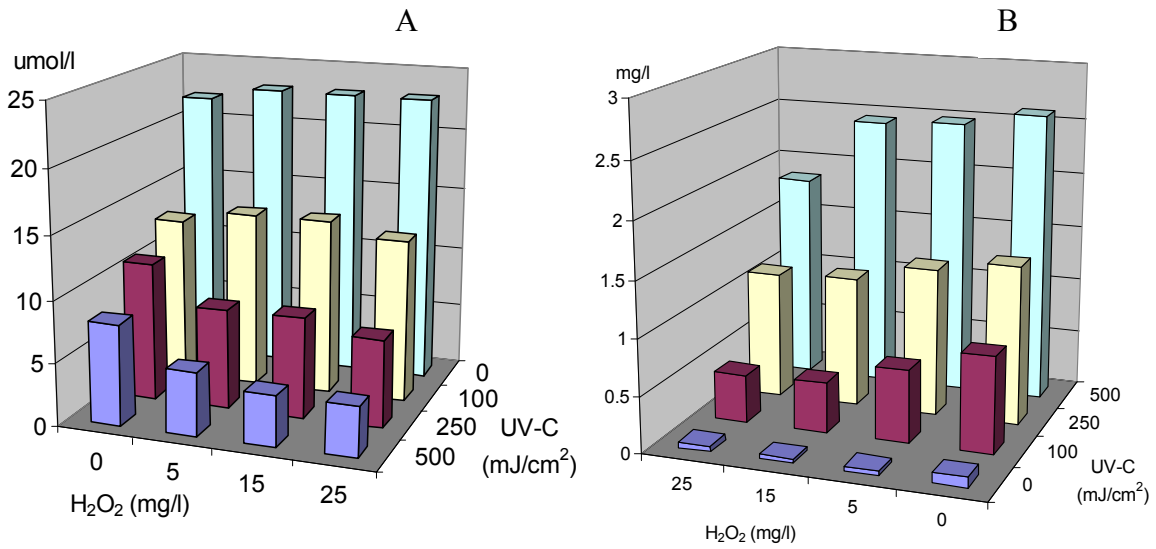

Fig. 4. (A) Break down of iron chelate (May 17) as caused by H_2O_2 and UV-C. (B) Build-up of nitrite (April 7) as caused by H_2O_2 and UV-C.