

REMEDICATION OF RESIDUES ON STORED PRODUCT SURFACES USING OZONE-BASED FUMIGATIONS

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ABSTRACT

Evolving environmental and public health concerns surrounding non-target exposure of consumers to pesticide residues, regardless of concomitant toxicological evidence, necessitates the development of safe and effective methodologies for residue minimization. Ozone fumigation, alone and in combination with other gases, was explored as a means for degrading “undesirable” organic residues on stored products. Organic residues sorbed onto model abiotic glass surfaces or onto stored products were fumigated separately in a flow-through chamber at $150 - 900 \pm 10$ ppmv ($\mu\text{L L}^{-1}$) reagent gas. Heterogeneous rate constants of gaseous ozone, and its mixtures, reacting with a sorbed organic residue, k_{O_3} ($\text{M}^{-1} \text{min}^{-1}$), were calculated for all surface types. The kinetics and mechanism of residue removal, supported by gas chromatography- and liquid chromatography-mass spectrometry product analyses, is discussed in the context of facilitating compliance with maximum residue level (MRL) tolerances for stored products. Results indicate that the extent of residue reduction varies with chemical structure; however, most residues can be rapidly degraded via decomposition radicals from ozonide intermediates and subsequent chain reactions involving (e.g., $\cdot\text{OH}$, $\cdot\text{OOR}$, etc.). This study provokes a myriad of research opportunities that can be consistent with the overall goal of maximizing degradation of pesticide residues while minimizing unintended toxicity produced by “disinfection/remediation” technologies. Future work will focus on developing ozone fumigation as a remediation technology that is a more universally applicable tool for industries that use chemicals for pest control.

Key words: Ozone fumigation; residue mitigation; residue degradation

INTRODUCTION

Fungicides are applied to control plant diseases that reduce commodity yield, deteriorate quality, and pose a food-borne health risk to consumers (Elad et al., 2004; Sipsas and Kontoyiannis, 2008; Tournas, 2005; Barkai-Golan, 2001). In an initial assessment of the practical feasibility of using gaseous ozone for fungicide residue removal/remediation, the degradative potential of fungicides was comparatively evaluated. Specifically, we report the extent that residue levels of boscalid, iprodione, fenhexamid, cyprodinil, and pyrimethanil decreased on grapes following fumigation with gaseous ozone. Using model glass systems to isolate abiotic contributions toward degradation, we probed the mechanistic role of ozone in fungicide destruction using kinetic profiles and byproduct identification with gas

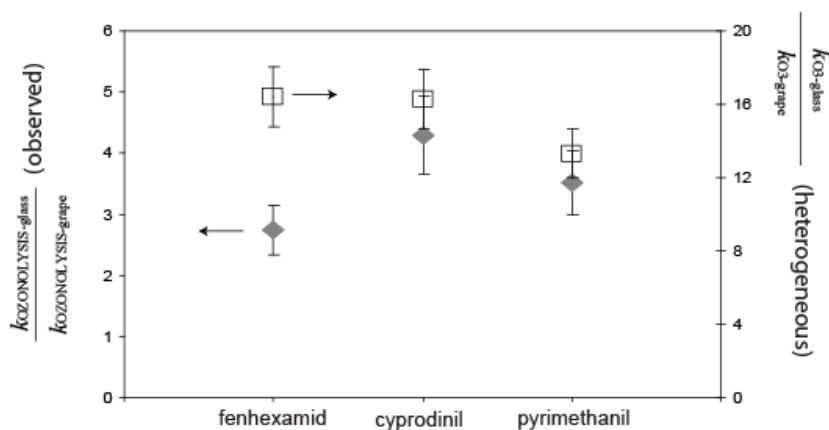
chromatography- and liquid chromatography-mass spectrometry (GC-MS and LC-MS, respectively).

MATERIALS AND METHODS

Experimental procedures are as described in Walse and Karaca (2011).

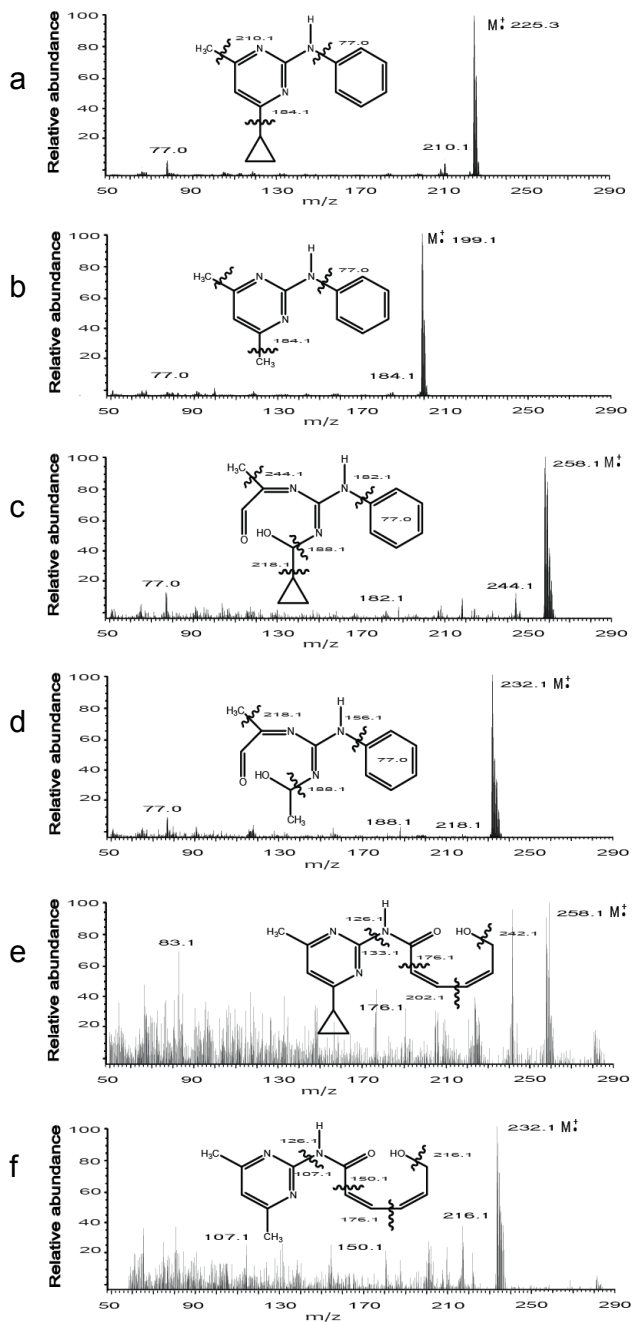
RESULTS AND DISCUSSION

Strategies must be developed for the remediation of pesticide residues on agricultural commodity, including stored product, when tolerances of maximum residue levels (MRLs) may not be exceeded. This study provides the first example of gaseous ozone being used in this context and provokes a myriad of research opportunities that can be consistent with the overall goal of maximizing degradation of pesticide residues while minimizing unintended toxicity produced by “disinfection/remediation” technologies. Results indicate that the extent of residue reduction varies with chemical structure, with some residues expected to undergo negligible degradation. However, pesticides amenable to ozonolysis can be rapidly degraded via decomposition radicals from ozonide intermediates and subsequent chain reactions. Future work will focus on developing ozone fumigation as a remediation technology that is a more universally applicable tool for industries that use chemicals for pest control; forthcoming manuscripts will detail efforts to circumvent the structurally selective nature of ozone by developing mixtures, in both the gas and solid phases, to maximize production of structurally indiscriminate radicals (e.g., $\cdot\text{OH}$, OOR, etc.) that facilitate decomposition of surface-sorbed pesticides (Palm et al., 1997; Palm et al., 1999; Pflieger et al., 2009). When considering fungicide degradation on fresh produce, technical aspects of ozone fumigation need to be refined and dovetailed with the infrastructural capabilities and challenges of commercial production as well as synchronized with the trade and environmental requirements facing agriculture.

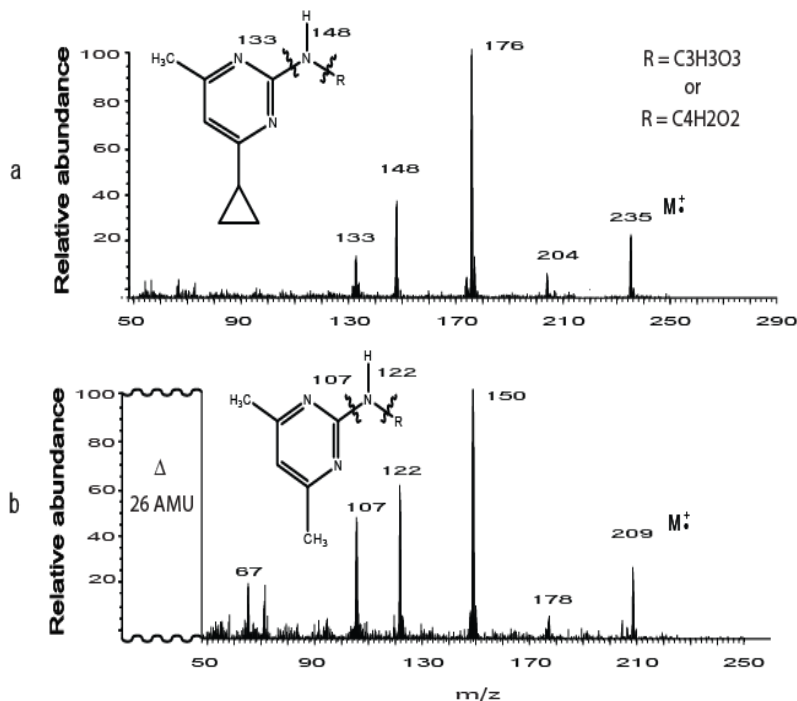


The glass to grape ratio of observable rate constants of ozonolysis, $k_{\text{OZONOLYSIS}}$, and heterogeneous rate constants of gaseous ozone reacting with a sorbed fungicide, k_{O_3} , which is corrected for $[\text{O}_3]_{\text{g}}$. Residue degradation proceeded ~ 15 -fold slower on stored product surfaces relative to glass, possibly due to preferential reaction of ozone with the stored

product surface and/or inert ingredients in the commercial formulations that limit access of ozone to reactive groups of the fungicides.



The 26 amu (C_2H_2) mass difference in between the structural analogs, cyprodinil (a, c, e) and pyrimethanil (b, d, f), was a convenient mass spectrometric diagnostic of reactivity for both the aniline and pyrimidine aromatic systems as shown above for GC-EIMS spectra.



Mechanistic support for the involvement of radical oxidants in the heterogeneous ozonolysis of residues stems from GC-EIMS identification of trace oxidative products with MWs of 235 and 209 for cyprodinil (a) and pyrimethanil (b), respectively, as confirmed by CI GC-MS (not shown); either two (i.e., $C_4H_2O_2$) or three oxygen atoms (i.e., $C_3H_3O_3$) were added to the aniline group in a manner that is not consistent with dicarbonyl addition in either 1-2 (α) or 1-4 (γ) orientation.

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