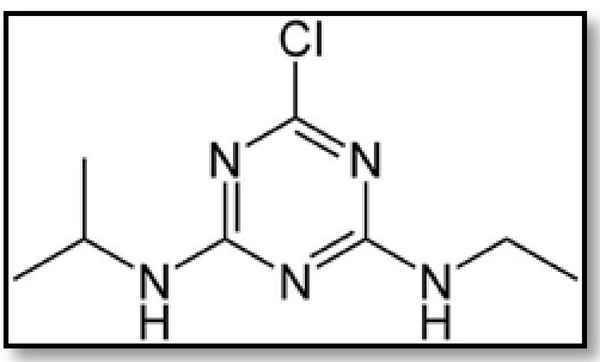
OZONE CASE STUDY
Industrial Chemical Blending Facility
Sunnyvale, California

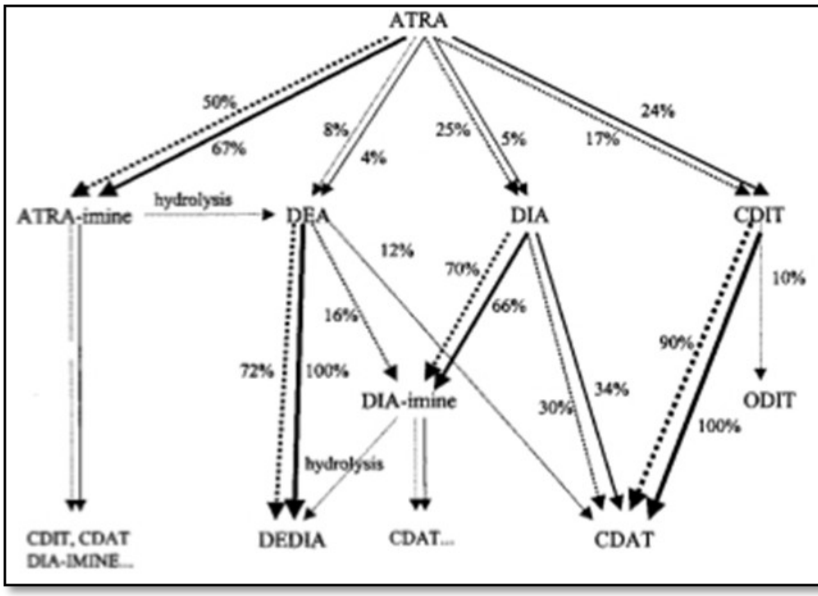
Pesticides are applied all over the world in order to effectively deter, eradicate or control pests that are harmful to humans, livestock, and the growth of agricultural crops. However, utilization of these organic compounds does not come without detrimental effects to our surroundings. Extensive use of pesticides has caused widespread environmental contamination, and exposure to high concentrations of these chemicals can be detrimental to the human population.[1] [1] Due to their durability, volatility, and ability to be easily spread throughout the environment, pesticides have become persistent in residual groundwater and drinking water sources through surface run-off from agricultural land, direct application, spray drift, erosion, and spills.[1] Pesticide residues collect in groundwater and aquifer sources, eventually reaching potentially hazardous and toxic concentrations. Regulations limiting pesticide concentrations have established safe limits in order to limit human risk and environmental pollution.[1] In order to maintain nontoxic levels of these compounds, numerous chemical and biological remediation methods have been applied to reduce pesticide presence in the soil and its sur-

Due to its strong oxidation potential (2.1V), ozone, and additional Advanced Oxidation processes have often been used as an effective means of chemical pesticide remediation from ground and drinking water sources. Atrazine, also known as 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine, is one of the most widely used agricultural herbicides in the world today.[2] Due to its persistent nature and high usage, traces of atrazine herbicides are found in many ground and surface waters. A study conducted by Acero, Stemmler, and von Gunten investigated the resulting products of reactions between atrazine and both molecular ozone and hydroxyl radicals (AOP). It was noted that when compared to molecular ozone, Advanced Oxidation Processes were proven to be more effective in the elimination of not only atrazine, but its first degradation by-products as well.[2] When reacted with molecular ozone, atrazine produced ATRA-imine and CDIT as prominent degradation products. DEA and DIA were also produced in small amounts.[2] These four primary degradation products then further reacted with ozone to produce secondary degradation products including DEDIA, CDAT, ODIT, DIA-imine, acetamide, and CDIT. Advanced Oxidation Processes resulted in similar degradation products as direct ozonation.[2]



Atrazine molecule

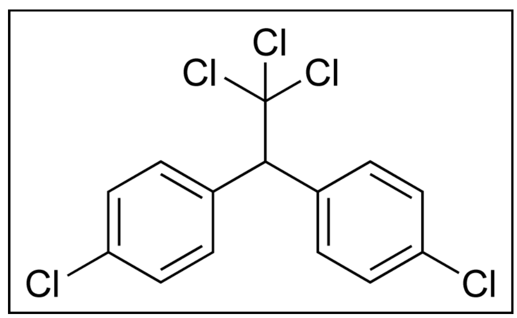
Kinetic studies comparing reaction rates of atrazine and its degradation products with both ozone and the OH radical, revealed rate constants of approximately 0.1 M^{-1} s^{-1} and 1.2E9 M^{-1} s^{-1}, respectively.[2] The large degree of magnitude between these rate constants demonstrates the speed and effectiveness of the highly reactive hydroxyl radical produced from AOP. Figure 1, taken from the aforementioned Acero study, illustrates degradation product pathways resulting from reactions of atrazine with ozone and AOP.



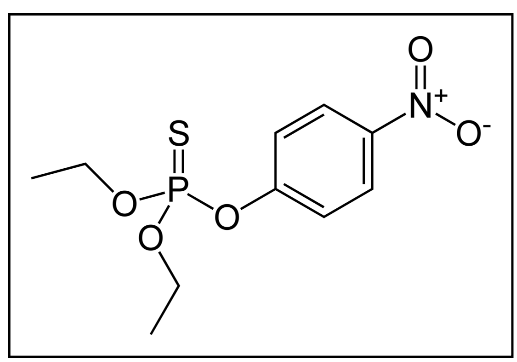
Reaction pathways for molecular ozone and hydroxyl radical reactions are shown with percentages representing relative importance of the pathway. Solid lines represent molecular ozone reactions and dashed lines represent OH radical reactions.[2]

Pesticides are often classified into five main groups: chlorinated hydrocarbons, organophosphorus compounds, phenoylalkyl acid derivatives, organonitrogen compounds, and phenolic compounds.[3] A 1989 study by Reynolds extensively covers the degree of reactivity and reaction product compounds when ozone is reacted with compounds in each of these five categories.

Chlorinated hydrocarbons include compounds such as DDT, aldrin, dieldrin, heptachlor, and endosulphan. While conflicting data exists on the extent of the reaction of these compounds with ozone, most chlorinated hydrocarbons recorded reactivity ranging from slight to substantial.[3] Endosulfan and heptachlor epoxide were exceptional. However, reaction products were unable to be well identified in these studies.[3] Unlike their chlorinated hydrocarbon cousins, organophosphorus compounds such as DDTP, dimefox, menthion, parathion, and malathion have been proven to react positively to ozonation. Oxons, phosphoric and succinic acid derivatives, and nitrophenols are the main products



DDT molecule



Parathion molecule

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Phenoxyalkyl acid derivatives (2,4-D, 2,4,5-T, MCPA, MCPB) also degrade when exposed to ozone oxidation. Herbicides 1,4-D, MCPA, and MCPB undergo rapid and virtually complete destruction when oxidized with ozone, while 2,4,5-T only experiences limited removal.[3] Short carbon chain aliphatic acids, carbon dioxide and chloride ions have been identified as common products.[3]

Organonitrogen compounds including atrazine, amitrole, fenuron, and diuron also experience virtually complete removal when brought in contact with molecular ozone.[3] Oxidation of five and six membered N-heterocyclic organonitrogen compounds results in triazine derivative product compounds.[3]

Lastly, phenolic compounds (Akrox, Karatan, o-nitrophenol, DNMP, pentachlorophenol) also successfully undergo complete oxidation.[3] Inorganic anion products such as nitrates and chlorides have been identified as main products in pentachlorophenol oxidation, while dinitrophenols and alcohols have been present following ozonation of Akrox and Karatan.[3]

Despite the relative success of ozone and Advanced Oxidation Process remediation techniques in the removal of pesticide, we must keep in mind that the effectiveness of ozone treatment is easily affected by numerous variables. pH elevation and increased ozone contact time have been observed to positively influence the effects of ozone with pesticide compounds.[3] Humic substances—which comprise a major component of natural organic matter (NOM) in soil and water—and free radical scavenger bicarbonate ions can both decrease pesticide-ozone reaction rates.[3] With these variables in mind, Piper Environmental Group, Inc. can easily craft an appropriate ozone or Advanced Oxidation system to remediate elevated pesticide concentra-

[1] Salama, A. K., & Osman, K. A. (2013). Remediation of Pesticide-Polluted Water using Ozonation as a Safe Method. *Global Journal of Human Social Science Geography, Geo-Sciences & Environmental Science & Disaster Management*, *13*(2), 11-17.
[2] Acero, J. L., Stemmler, K., & von Gunten, U. (2000). Degradation Kinetics of Atrazine and Its Degradation Products with Ozone and OH Radicals: A Predictive Tool for Drinking Water Treatment. *Environ. Sci. Technol.*, *34*(4), 591-597.
[3] Reynolds, G., Graham, N., Perry, R., & Rice, R. G. (1989). Aqueous Ozonation of Pesticides: A Review. *Ozone Science & Engineering*, *11*, 339-382.

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