Article

Comprehensive Screening Study of Pesticide Degradation via Oxidation and Hydrolysis

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ABSTRACT: This comprehensive study focused on the reactivity of a set of 62 pesticides via oxidization by free chlorine, monochloramine, chlorine dioxide, hydrogen peroxide, ozone, and permanganate; photodegradation with UV_{254}; and hydrolysis at pH 2, 7, and 12. Samples were analyzed using direct injection liquid chromatography–mass spectrometry detection or gas chromatography–electron capture detection after liquid–liquid extraction. Many pesticides were reactive via hydrolysis and/or chlorination and ozonation mechanisms under typical drinking water treatment conditions, with less reactivity exhibited on average for chlorine dioxide, monochloramine, hydrogen peroxide, and UV_{254}. The pyrazole and organophosphorous pesticides were most reactive in general, whereas carbamates and others were less reactive. The screening study provides guidance for the pesticide/oxidation systems that are most likely to lead to degrades in water treatment and the environment.

KEYWORDS: pesticide degradation, oxidation, photodegradation, hydrolysis, drinking water

INTRODUCTION

The widespread use of pesticides in conventional farming practices and modern civilization has led to the increased occurrence of pesticide residues in drinking water supplies. Whereas pesticide applications are most often cited as agricultural, urban usage for private home pest control, golf course maintenance, and municipal pest management also contributes significantly to pesticide pollution in water supplies. Studies over the past few decades have documented the occurrence of pesticides and their degrades in a wide variety of water supplies. Drain-field and stormwater runoff, both urban and agricultural,[1,2] surface water,[3–5] groundwater,[6–10] and finished drinking water[11] are the most important for drinking water supplies due to their potential or direct purpose as a potable water source. Studies also indicate that pesticide pollution can have indirect impacts on drinking water through air,[12] rainfall,[13] and snowfall.[14]

Degradation of these pesticides may occur in the environment by hydrolysis and photolysis and additionally via oxidation (and reduction) in water and wastewater treatment. Various treatment processes are utilized to remove chemical and biological contaminants from potable water. Studies to date have focused on the removal and/or reactivity of a single or small set of pesticides with a limited number of treatment processes. These studies indicate that many different treatments show the potential for inducing degrade formation through chemical oxidation with disinfectants, photolysis with ultraviolet, hydrolysis at high pH, biodegradation, and ozone.[15–23] The toxicity of degrades can potentially be greater than the parent with respect to ecotoxicity[24,25] and for humans (e.g., for oxon degrades of organoposphate pesticides[26]).

The purpose of this study was to identify combinations of 62 pesticides and 6 oxidants (i.e., free chlorine, monochloramine, chlorine dioxide, permanganate, ozone, and hydrogen peroxide), UV, and pH that are most reactive, leading to pesticide degrade formation under typical disinfection exposures (i.e., concentration (C) times time (t), or "CT") and environmental conditions. This information is important to help focus future work on degrade identification, kinetic modeling, occurrence, and toxicity.

EXPERIMENTAL PROCEDURES

Chemicals. All treatment chemicals (sodium hypochlorite, ammonium chloride, etc.) and solvents (e.g., hexane) were of at least reagent grade and were obtained from Fisher Scientific (Fair Lawn, NJ). The pesticides investigated in this study were purchased from Sigma-Aldrich (St. Louis, MO). Pesticide stock solutions were freshly prepared and stored in amber bottles to prevent possible light-induced decomposition. Laboratory water (Milli-Q or MQ) with resistivity >18.2 MΩ·cm was produced by a water purification system (model Simplicity 185, Millipore Co., Bedford, MA) to prepare working solutions.

Experimental Methods. *Experimental Design.* The experiments were divided into two main groups, GC compounds and LC compounds, depending on which analytical method was most appropriate. For GC compounds, samples were prepared from five standard mixes (G1–G5) as listed in Table 1. Stock solutions of mixes G1, G2, and G4 were purchased from Sigma-Aldrich at individual pesticide concentrations of 500, 500, and 1000 mg/L, respectively.

Table 1. Hexane LLE Percent Recoveries, Standard Deviation of Recoveries, and MDLs for 36 Compounds Analyzed by GC-ECD

compound	mix	mean recovery (%)	recovery RSD (%)	MDL (ng/L)
acetochlor	G3	100.6	10.6	97.4
alachlor	G1	102.0	22.8	57.9
aldrin	G1	107.8	26.5	91.8
chloradane (α)	G2	98.9	9.8	82.5
chloradane (γ)	G2	98.5	17.4	80.4
chlorobenzilate	G4	103.6	11.2	96.8
chloroneb	G4	99.4	7.4	76.3
chlorothalonil	G4	121.6	10.7	37.0
chlorpyriphos	G5	102.1	10.1	99.0
dacthal	G4	105.1	4.6	57.9
diazinon	G3	99.1	7.2	117.6
dieldrin	G1	104.0	13.3	78.8
dimethenamid	G3	105.4	9.7	12.5
endrin	G2	100.2	9.9	71.5
etridiazole	G4	104.0	3.5	37.1
fonofos	G3	99.1	9.2	85.4
heptachlor	G2	94.5	12.9	39.0
heptachlor epoxide	G2	95.7	11.3	69.8
hexachlorbenzene	G2	132.0	31.6	129.3
hexachloropentadiene	G2	97.3	18.0	94.7
isoxaflutole	G3	94.7	9.7	82.5
lindane	G1	105.8	15.4	69.5
linuron	G3	115.6	45.6	97.0
malathion	G5	101.4	22.4	100.7
methoxychlor	G2	85.5	12.4	96.1
metolachlor	G3	99.8	8.6	120.6
metribuzin	G5	108.2	27.5	115.4
nonachlor (*cis*)	G1	93.1	26.7	81.8
nonachlor (*trans*)	G1	104.9	20.5	65.4
parathion	G5	104.1	17.9	138.8
pendimethalin	G5	97.5	11.1	84.3
permethrin	G4	84.6	17.2	63.9
propachlor	G4	100.4	4.3	53.0
propanil	G3	125.9	42.0	97.3
terbufos	G5	94.7	10.7	110.5
triflualin	G4	112.3	11.8	67.1

Stock solutions of mixes G3 and G5 were prepared with concentrations of each pesticide at 191 and 179 mg/L, respectively.

For LC compounds, samples were prepared from four standard mixes (L1−L4), as listed in Table 2. Stock solutions of mix L2 were purchased from Sigma-Aldrich at individual pesticide concentrations of 100 mg/L. Stock solutions of mixes L1, L3, and L4 were prepared with concentrations of each pesticide at 52 mg/L, 100 mg/L, and 77.8 mg/L, respectively.

Experiments were conducted in 5−10 mM sodium phosphate buffered laboratory water at 23 ± 1 °C at pH 6.6 and 8.6 in 250 mL amber glass chemical reactors. A shaker table was used for mixing at 200 rpm. GC compound experiments were initiated by adding a stock pesticide mix solution to an initial concentration of 1.5−3 μg/L of each study compound, mixing, and then removing a 35 mL sample for initial concentration determination. For LC compound experiments, an initial concentration of 25 μg/L and a 1 mL sample volume were used.

Next, the remaining solution was spiked with an oxidant, subjected to hydrolysis by pH adjustment, or subjected to UV photolysis at 254 nm. For LC compounds, 1 mL samples were periodically taken from the reactor and immediately injected into the LC-MS for immediate analysis. The injection time was recorded as the quench time due to immediate chromatographic separation of the oxidant from the

Table 2. MDLs for 26 Compounds Analyzed by LC-MS

compound	mix	MDL (ng/L)
2,4,5-TP	L3	141.8
2,4-D	L3	216.3
3-hydroxycarbofuran	L2	203.7
aldicarb	L2	187.3
aldicarb sulfone	L2	351.7
aldicarb sulfoxide	L2	164.5
atrazine	L1	20.9
bentazon	L3	230.1
carbaryl	L2	344.8
carbofuran	L2	398.4
cyanazine	L1	64.9
dicamba	L3	98.5
diuron	L1	106.9
endothall	L3	100.3
EPTC	L1	80.2
fipronil	L4	492.6
fluometuron	L1	75.5
methiocarb	L2	367.8
methomyl	L2	197.9
molinate	L1	77.8
oxamyl	L2	262.9
picloram	L3	247.6
prometon	L1	79.9
propazine	L1	16.3
propoxur	L2	301.7
simazine	L1	50.8

analytes. From 7 to 10 samples were taken over various time intervals, depending on the rate of reaction for a given oxidant or condition.

For GC compounds, a 35 mL sample was withdrawn after a predetermined time interval (chosen to achieve an oxidant exposure representative of typical drinking water treatment conditions) and then extracted using the hexane LLE method (quenching any further reaction). All processed samples were stored in the dark at −20 °C and injected within 36 h. Oxidant concentrations, pH, and/or UV energy were periodically monitored to allow determination of exposures.

Eight common oxidation/disinfection processes were evaluated in this study, including oxidation with free chlorine (FC), monochloramine (MCA), chlorine dioxide (ClO$_2$), ozone (O$_3$), permanganate (MnO$_4^-$), ultraviolet light (UV), hydrogen peroxide (H$_2$O$_2$), and hydrolysis at pH 2, 7, and 12 (HYD2, HYD7, and HYD12, respectively). The methods used for oxidant stock preparation are described below.

Free Chlorine. FC stock solutions were prepared by dilution from a 5% sodium hypochlorite solution (Fisher Scientific). FC was determined by the difference between total chlorine concentration (as determined with Hach DPD method 8167 using Accuvacs; Loveland, CO) and the monochloramine concentrations (determined with HACH Nitrogen, Free Ammonia, and Chloramine (Mono) Indophenol Method 10200).

The typical CT value for 3-log (99.9%) removal of *Giardia Cysts* using FC at pH 6−9 ranges from 24 to 146 mg·min/L at temperatures from 20 to 25 °C.[27] A typical range for the FC concentration used during drinking water disinfection is 0.2−2 mg/L.[28] The CT values used for this study ranged from 107 to 173 mg·min/L using FC concentrations of 2−5 mg/L as Cl$_2$.

Monochloramine. MCA stock solutions were prepared from sodium hypochlorite and ammonium chloride at a slight excess molar ratio of 1.05:1 (ammonium/hypochlorite) at pH >9 (as described in ref 29). Stable, high-concentration substocks solutions of NaOCl and NH$_4$Cl for MCA stock preparation were prepared and stored in the dark. During stock MCA creation, the pH was controlled to maintain a pH of 9.0 or greater by utilizing phosphate-buffered water, monitoring pH, and adding sodium hydroxide as needed.

The presence of a slight excess of ammonia was confirmed in the MCA stock solution using an ammonia probe (model Orion 9512, Thermo-Electron Corp., Waltham, MA) to ensure that the MCA stock solution contained no FC. Additionally, absorbance scans of the MCA stock solution at pH 9.0 were also prepared from 200 to 400 nm to confirm the absence of FC. During experiments with MCA, the pH was controlled to maintain a pH of either 6.6 or 8.6 by utilizing phosphate-buffered water and monitoring pH. MCA concentrations during experiments were determined using Hach Nitrogen, Free Ammonia, and Chloramine (Mono) Indophenol Method 10200 using chemicals obtained from the Hach Co. (Loveland, CO).

The typical CT value for 3-log (99.9%) removal of *Giardia Cysts* using chloramines at pH 6−9 ranges from 750 mg·min/L at 25 °C to 1100 mg·min/L at 20 °C.[27] A typical range of concentrations used during drinking water disinfection is 1−4 mg/L.[28] The CT values used for this study ranged from 1287 to 1430 mg·min/L using MCA concentrations of 9−14 mg/L as NH_2Cl.

Permanganate (MnO_4^-). Permanganate stock solutions were prepared by dissolving potassium permanganate solid in laboratory water. The permanganate concentration was determined using Hach DPD Method 8167 using Accuvac ampules.

Permanganate is not commonly used as a disinfectant, but is used to control taste and odor compounds or to oxidize reduced manganese at concentrations in the range of 0.2−20 mg/L. Permanganate has also been shown to control Asiatic clams and zebra mussels at concentrations of 1.1−4.8 and 0.5−2.5 mg/L, respectively.[28] The CT values used for this study ranged from 134 to 164 mg·min/L using permanganate concentrations of 3−5 mg/L as MnO_4^-.

Chlorine Dioxide. Gaseous ClO_2 was produced using a CDG Bench Scale ClO_2 Generator (CDG, Bethlehem, PA). The gaseous chlorine dioxide stream was bubbled into phosphate-buffered laboratory water. The ClO_2 concentration was measured by absorbance at 359 nm with a UV−vis spectrophotometer (Cary 50 Conc., Varian).

The typical CT value for 3-log (99.9%) removal of *Giardia* cysts using ClO_2 at pH 6−9 ranges from 11 to 15 mg·min/L at a temperature of 20−25 °C.[27] A typical range of concentrations used during drinking water disinfection is 0.07−2 mg/L.[28] The CT values used for this study ranged from 38 to 73 mg·min/L using ClO_2 concentrations of 2−3 mg/L as ClO_2.

Hydrogen Peroxide. H_2O_2 stock solutions were prepared by dilution of a 30% H_2O_2. H_2O_2 is not typically utilized independently for drinking water disinfection, but rather in conjunction with UV or ozone as an advanced oxidation process. The CT values used for H_2O_2 in this study ranged from 933 to 1100 mg·min/L using H_2O_2 concentrations of 100 mg/L as H_2O_2.

Ozone. Gaseous O_3 was produced from compressed oxygen using a corona discharge ozone generator (model GLS-1, PCI-WEDECO Environmental Technologies, West Caldwell, NJ). The gaseous O_3 stream was bubbled into phosphate-buffered laboratory water to create the ozone stock solution. O_3 concentration was measured using UV absorbance at 260 nm. The O_3 stock was then spiked into the samples and allowed to naturally degrade while being orbitally mixed at 200 rpm for 2 h. O_3 dosing was conducted in duplicate with one sample being used to monitor the O_3 concentration decay for calculation of CT (concentration × time) and the other used for subsequent chemical analysis. Samples were extracted as previously described.

The typical CT value for 3-log (99.9%) removal of *Giardia* cysts using O_3 at pH 6−9 ranges from 0.48 to 0.72 mg·min/L at a temperature of 20−25 °C.[27] A typical range of O_3 concentration used during drinking water disinfection is <0.1−1 mg/L.[28] The CT values used for this study ranged from 0.2 to 0.3 mg·min/L using ozone concentrations of 1−2 mg/L as O_3.

Ultraviolet Radiation. UV radiation was produced using a 1 W low-pressure narrow-band (254 nm) mercury vapor lamp (Pen Ray model 90-0004-01) situated along the midline of the 25 mm diameter, 6.6 cm long annular reactor. All nonsubmerged portions of the lamp were covered using Teflon tape to eliminate UV exposure from the surface. The exposures utilized in these experiments were based on the farthest point within the reactor receiving the desired

dosage. A typical CT value for 3-log (99.9%) removal of viruses is 36 mW·s/cm².[28] The CT values used for this study ranged from 77 to 97 mW·s/cm².

Hydrolysis at pH 2, 7, and 12. Reaction media for hydrolysis experiments was 10 mM sodium phosphate-buffered laboratory water at pH 2, 7, or 12. Samples were separated into individual 35 mL samples and tumbled for up to 7 days. A 35 mL sample was sacrificed for each condition/mix at 0 and 7 days. Samples were then extracted as previously described. pH was monitored throughout.

Instrumentation and Sample Processing. *Liquid−Liquid Extraction (LLE) for GC-ECD Analysis.* For LLE, a 35 mL sample was spiked with 50 μL of a surrogate stock (5 mg/L decachlor-obiphenyl (DCB) in acetone) and vigorously hand mixed for 10 s. A volume of 2 mL of hexane and 6 g of sodium sulfate were then added to the 35 mL sample with surrogate and mixed vigorously for 1 min. After phase separation, exactly 1 mL of the hexane layer was pipetted into a 2 mL amber autosampler vial and then spiked with 10 μL of an internal standard (2 mg/L pentachloronitrobenzene (PCNB) in hexane for mixes G1, G2, and G4 or 2 mg/L 2,4,5,6-tetrachloroxylene (TCX) in acetone for mixes G3 and G5). The vial was capped and vortexed to ensure mixing. All samples were stored at −20 °C until analyzed.

Gas Chromatography−Electron Capture Detector (GC-ECD). Sample extraction and analysis with GC-ECD utilized U.S. EPA method 505, slightly modified as described below. Analysis was using a Hewlett-Packard/Agilent 5890 series gas chromatograph equipped with an ECD and 6890 series injector or an Agilent Technologies 6890N series gas GC equipped with a μ-ECD and 7683 series injector (Palo Alto, CA). The carrier gas was nitrogen at a rate of 2 mL/min. For the 5890 and 6890 methods, a 2 or 1 μL sample, respectively, was injected at from 250 °C (mixes G1, G2, and G4) to 280 °C (mixes G3 and G5) in splitless mode onto a HP-5MS capillary column from Agilent (30 m × 0.25 mm i.d., 0.25 μm film thickness).

The temperature gradient for mixes G1, G2, and G4 was 1 min at 80 °C, 20 °C/min ramp to 170 °C, 2 °C/min to 185 °C, 1 min at 185 °C, 15 °C/min ramp to 290 °C, and 6 min at 290 °C. The temperature gradient for mixes G3 and G5 was 1 min at 50 °C, 30 °C/min ramp to 180 °C, 3 °C/min ramp to 205 °C, 4 min at 205 °C, 20 °C/min ramp to 290 °C, and 6 min at 290 °C. The detector temperature was set at 300 °C for all mixes.

Additional compound confirmation was achieved using an Agilent Technologies 6893 series GC with a 5973 mass selective detector and a 7673 autosampler utilizing the same chromatography conditions as for the GC-ECD methods. Carrier gas flows varied between the GC-ECD and the GC-MS instruments, so that relative retention times and peak order were used for confirmation. The combined information of relative retention time and the various concentration peaks were used for compound verification. The chromatograms for each study compound mix are shown in Figure 1.

Liquid Chromatography−Mass Spectrometry (LC-MS). Pesticides were chromatographically separated using an Agilent 1100 series LC-MSD System (G1946D), which included a solvent degassing unit, a binary high-pressure gradient pump, an automatic sample injector, a column thermostat and unit, and a 1946D SL model mass spectrometer. A sample volume of 20 μL was injected. All columns were preceded by a SecurityGuard C-18 guard column/cartridge. Mixes L1 and L2 utilized a 150 × 3.0 mm Phenomenex Luna 3 μm Phenyl Hexyl column; mix L3 used a 150 × 3.0 mm Supelco Discovery 5 μm C18 column; and mix L4 used a 150 × 3.0 mm Phenomenex Synergi 4u Fusion-RP 80A 4 μm column. The columns were maintained at 30 °C for mixes L1 and L2; at 50 °C for mix L3; and at 25 °C for mix L4, with each at a flow rate of 0.3 mL/min. For mixes L1 and L2, a binary gradient utilized solvent A (MQ water with 0.1% nitric acid) and solvent B (acetonitrile with 0.1% nitric acid). The gradient used was 0% solvent B, ramping to 40% at 5 min, to 60% at 10 min, to 80% at 15 min, and to 100% at 18 min, at which it was held for 2 min and then decreased to 0% at 20 min and held for 5 min. Mix L2 used a binary gradient where solvent A was MQ water with 0.04% acetic acid and solvent B was acetonitrile. Solvent B started at 0%, then ramped to 90% over 20 min, then back to 0% over 0.5 min, at which it
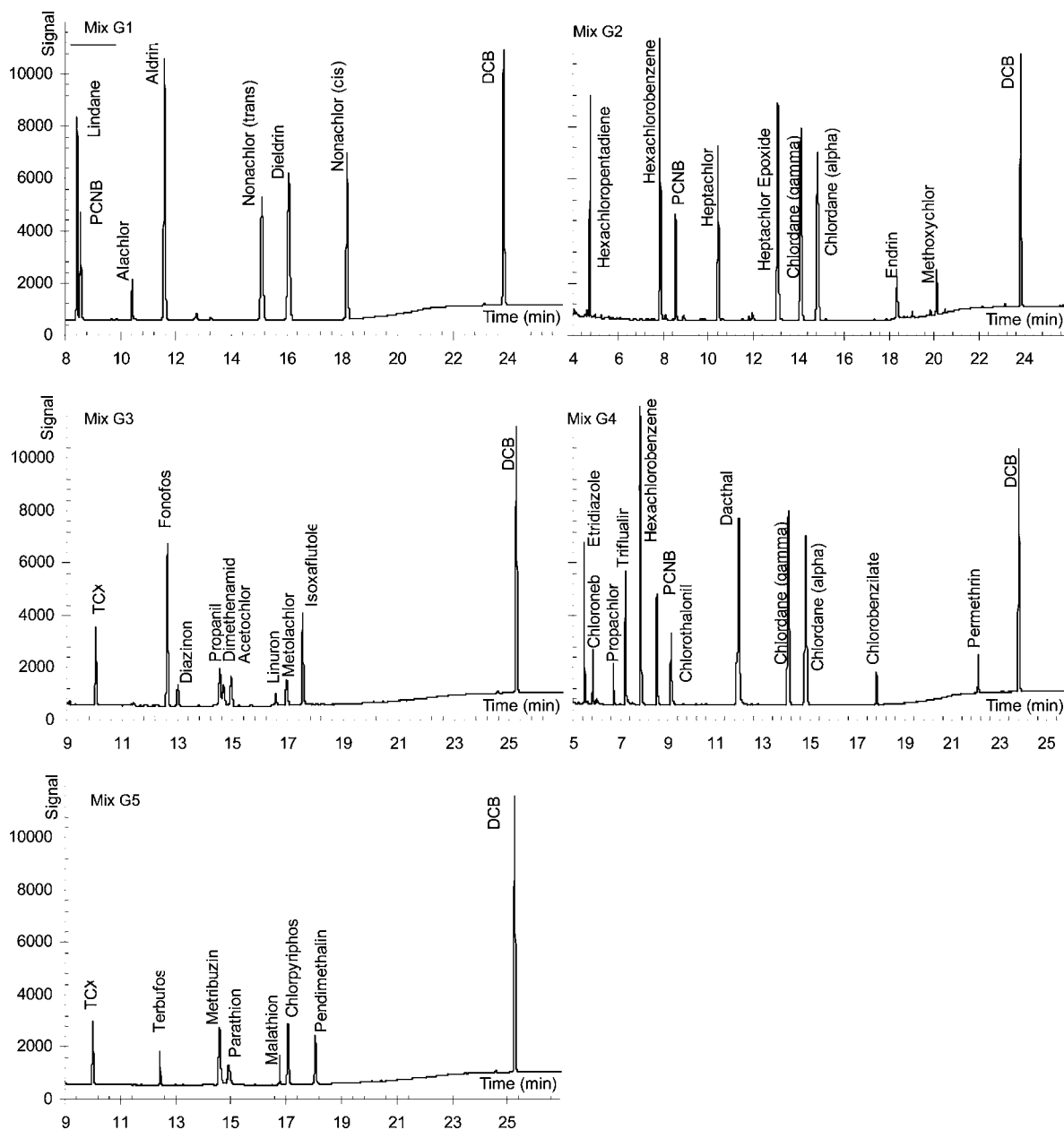
Figure 1. Chromatograms for GC-ECD analysis of study compounds including internal standards (PCNB and TCX) and surrogate (DCB). Pesticide compounds were at 30 μg/L.

was held for 4.5 min. Mix L4 used a binary gradient where solvent A was MQ water with 0.04% acetic acid and solvent B was methanol. Solvent B started at 70% and was held there for 3 min, then ramped to 100% over 6 min, and held for 8 min, prior to being ramped back to 70% over 0.5 min and held for 3.5 min.

For mixes L1 and L2, the mass spectrometry utilized a positive ion electrospray mode in selected ion monitoring (SIM) mode, with the nebulizer pressure set at 35 psig, the capillary set at 3500 V, a drying temperature of 250 °C, a drying gas flow of 12 L/min, and the fragmentor set at 75−130 V (depending on the compound). For mixes L3 and L4, the mass spectrometry utilized a negative ion electrospray mode in SIM mode, with the nebulizer pressure set at 35 psig, the capillary set at 3500 V, a drying temperature of 300 °C, a drying gas flow of 12 L/min, and the fragmentor set at 65−80 V (depending on the compound). The chromatograms for each study compound mix are shown in Figure 2.

Recoveries, Standard Curves, Method Detection Limits (MDLs), and Duplication. For GC-ECD compounds, the MDL ranged from 12.5 to 139 ng/L after LLE with an average percent

recovery was 102.3% in laboratory water for the 36 compounds extracted. Average compound recoveries fall within the commonly accepted 70−120% range, with the exceptions of chlorothalonil (121.6%), hexachlorobenzene (132.0%), and propanil (125.9%) (Table 1).

The average relative standard deviation (RSD, %) of the response of surrogate compound, DCB, divided by the internal standard response for all samples included in the study (i.e., experiments, recovery, and standard curves) was 11.8%, indicating consistent recoveries for extraction and replication of experiments. For experiments, the average %RSD between duplicate experiments was 8.9%, indicating consistent removals and precision between experiments.

All standard curves were at least six-point linear curves with a regression coefficient (R^2) >0.995, indicating good linearity over the range of concentrations investigated.

MDLs were determined via standard methods by injecting the seven separate samples, at an estimated 3 times the anticipated MDL, and multiplying the standard deviation of the concentration by 3.14. For experiments, the average %RSD between duplicate experiments was
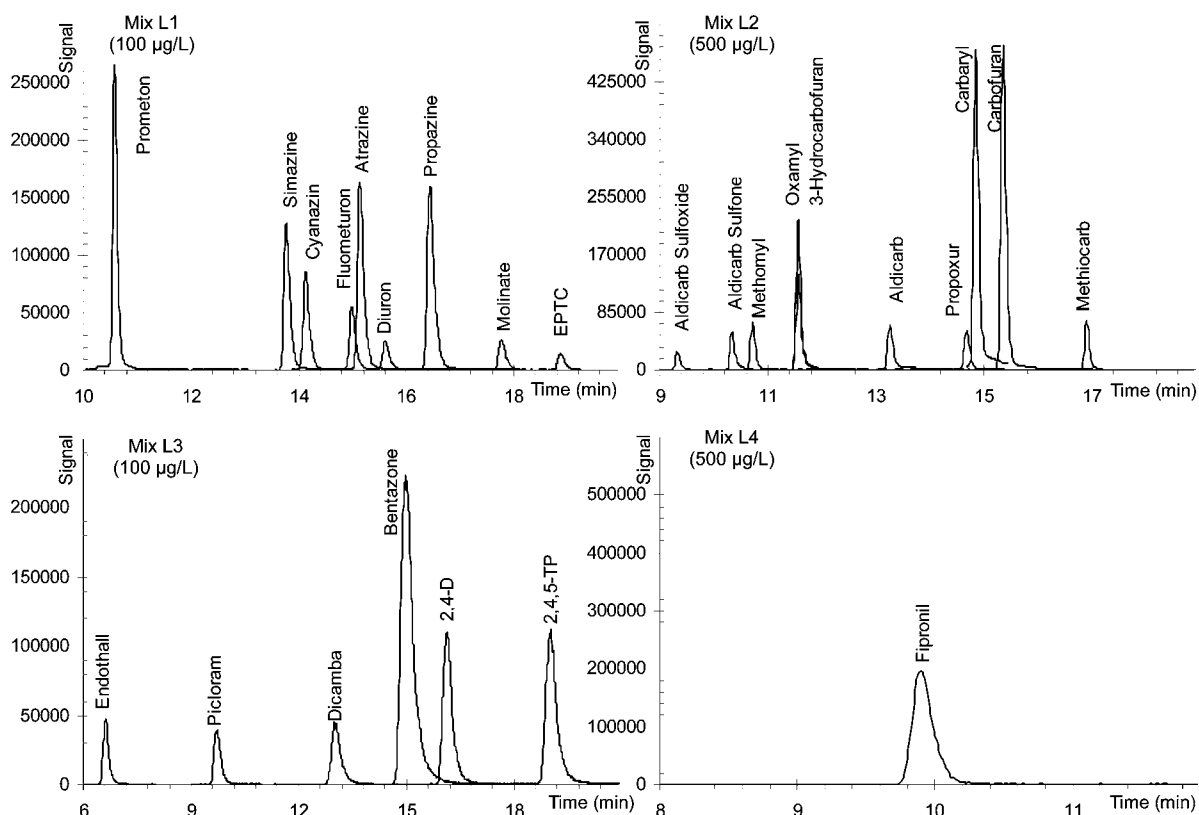
Figure 2. Chromatograms for LC-MS analysis of study compounds including internal standards (PCNB and TCX) and surrogate (DCB). Pesticide compounds were at 30 μg/L.

2.6%. The MDL for direct injection LC-MS for each compound ranged from 16.2 to 492.6 ng/L (Table 2).

Quenching. For LC compounds, injection into the column provided immediate quenching for oxidation experiments (with free chlorine, monochloramine, chlorine dioxide, hydrogen peroxide, and permanganate). Ozone was allowed to completely decay while tracking ozone concentration in order to calculate exposure (mg·L/min).

For GC compounds, extraction of compounds into the hexane phase served as the quenching step for oxidation experiments with FC, MCA, ClO_2, H_2O_2, and MnO_4^-. Separate experiments demonstrated negligible oxidant reactivity with the pesticides, internal standard, and surrogate compounds in the hexane phase.

■ RESULTS AND DISCUSSION

Overall Trends of Treatments. The results of the screening experiments showed a wide range of reactivities for pesticides by oxidants, hydrolysis, and UV_{254} under drinking water treatment conditions. Table 3 lists the compounds studied by class and their reactivity with each oxidant and/or condition, grouped with designations of H ("high") for >50% removal, M ("moderate") for between 20 and 50% removal, and L ("low") for <20% removal of the study compound. Considering only compounds with the high reactivity classification (i.e., >50% removal under typical conditions), the order of reactivity of the study compounds was (Table 3) as follows: (hydrolysis)$_{high\ pH}$ > O_3 > FC > (hydrolysis)$_{low\ pH}$ > ClO_2 > MnO_4^- > MCA > (H_2O_2 = UV_{254}).

Combining compounds with either high or medium reactivity (i.e., >20% removal), the order of reactivity was (Table 3) (hydrolysis)$_{high\ pH}$ > O_3 > (hydrolysis)$_{low\ pH}$ > FC > ClO_2 > MnO_4^- > MCA > H_2O_2 > UV_{254}.

Thus, these results suggest conditions that may lead to greater parent removal, and the most significant degradate formation,

which may include excess lime softening (e.g., at pH 11.5), free chlorine, and ozone treatments. Specifically, for ozone, 29 and 23% of the pesticides were highly reactive with ozone at pH 6.6 and 8.6, respectively, whereas 23 and 21% were highly reactive with free chlorine at pH 6.6 and 8.6, respectively (Table 3). Of the 62 compounds studied, 90, 82−87, 92−97, and 97−98% had low reactivity with MCA, ClO_2, H_2O_2, and UV_{254}, respectively (Table 3).

Approximately half of the pesticides highly hydrolyzed at pH 12, a pH just slightly greater than the 11.3 commonly used for excess lime softening. More study of the extent of hydrolysis of these compounds in water treatment plants is warranted. Just 16 and 11% were highly hydrolyzed (unstable) at pH 2 and 7, respectively.

Over all the reactants, the classes of compounds having the highest percentage of highly reactive pesticides were (Table 3) pyrazole > organophosphorous > (triazinone, benzothiadiazole) > carbamate > others.

With FC, slightly higher reactivity was observed at lower pH consistent with the stronger oxidation power of hypochlorous acid as compared with hypochlorite (although speciation of the pesticide affects reactions rates as well). All of the organophosphorus compounds were highly reactive with FC, with aldrin, fipronil, hexachloropentadiene, and selected carbamates also showing high reactivity (Table 3). Only two carbamates, aldicarb and methiocarb, and two organophosphorus pesticides, fonofos and terbofos, were highly reactive with MCA. All other pesticides were recalcitrant to MCA except hexachloropentadiene and heptachlor.

ClO_2 was only highly reactive with fipronil and metribuzin at higher pH and aldicarb, methiocarb, fonofos, and turbofos at both pH levels (Table 3). ClO_2 was recalcitrant with all other

Table 3. Screening Study Results, Where H = >50% Removal, M = 20−50% Removal, and L = <20% Removal

compound	CAS Registry No.	class	method	FC pH 6.6	FC pH 8.6	MCA pH 6.6	MCA pH 8.6	ClO₂ pH 6.6	ClO₂ pH 8.6	MnO₄⁻ pH 6.6	MnO₄⁻ pH 8.6	H₂O₂ pH 6.6	H₂O₂ pH 8.6	O₃ pH 6.6	O₃ pH 8.6	UV pH 6.6	UV pH 8.6	hydrolysis pH 2	hydrolysis pH 7	hydrolysis pH 12
2,4,5-TP (Silvex)	93-72-1	acid	LC	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
2,4-D	94-75-7	acid	LC	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
dicamba	1918-00-9	acid	LC	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
endothal	62059-43-2	acid	LC	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
picloram	1918-02-1	acid	LC	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
acetochlor	34256-82-1	amide	GC	L	L	L	L	L	L	L	L	L	L	M	M	L	L	L	L	L
alachlor	15972-60-8	amide	GC	L	L	L	L	L	L	L	L	L	L	H	H	L	L	L	L	M
dimethenamid	87674-68-8	amide	GC	M	L	L	L	L	L	L	L	L	L	H	H	L	L	L	L	L
metolachlor	51218-45-2	amide	GC	L	L	L	L	L	L	L	L	L	L	M	M	L	L	L	L	L
propachlor	1918-16-7	amide	GC	L	L	L	L	L	L	L	L	L	L	L	L	L	L	M	M	L
propanil	709-98-8	amide	GC	L	L	L	L	L	L	L	L	L	L	M	M	L	L	M	M	M
bentazone	25057-89-0	benzothiadiazole	LC	L	L	L	L	H	H	L	L	L	L	H	H	L	L	M	L	M
aldicarb	116-06-3	carbamate	LC	H	H	H	H	H	H	L	M	L	L	H	H	L	L	H	M	H
aldicarb sulfone	1646-88-4	carbamate	LC	H	L	L	L	L	L	L	L	L	L	H	L	L	L	M	M	H
aldicarb sulfoxide	1646-87-3	carbamate	LC	H	H	L	L	L	L	H	H	L	L	L	L	L	L	H	M	H
carbaryl	63-25-2	carbamate	LC	L	H	L	L	L	L	L	L	L	L	M	H	L	L	M	H	H
carbofuran	1563-66-2	carbamate	LC	L	L	L	L	L	L	L	L	L	L	M	M	L	L	M	M	H
EPTC	759-94-4	Carbamate	LC	H	H	L	L	L	L	L	L	M	M	L	L	L	L	L	L	L
3 - hydroxycarbofuran	16655-82-6	carbamate	LC	L	L	L	L	L	L	L	L	L	L	M	L	L	L	M	M	H
methiocarb	2032-65-7	carbamate	LC	H	H	H	H	H	H	M	M	L	L	M	H	L	L	M	M	H
methomyl	16752-77-5	carbamate	LC	H	H	L	L	L	L	L	L	L	L	L	L	L	L	M	M	H
molinate	2212-67-1	carbamate	LC	H	H	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
oxamyl	23135-22-0	carbamate	LC	M	L	L	L	L	L	L	L	L	L	M	M	L	L	M	H	H
propoxur	114-26-1	carbamate	LC	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
pendimethalin	40487-42-1	dinitroaniline	GC	L	L	L	L	L	L	L	L	L	L	H	H	L	L	L	L	L
trifluralin	1582-09-8	dinitroaniline	GC	L	L	L	L	L	L	L	L	L	L	H	M	L	L	M	M	H
isoxaflutole	141112-29-0	isoxazole	GC	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	H
aldrin	309-00-2	organochloride	GC	H	M	L	L	L	H	H	H	L	M	H	H	M	M	H	H	H
chloradane (α)	5103-71-9	organochloride	GC	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	M
chloradane (γ)	5103-74-2	organochloride	GC	L	L	L	L	L	L	L	L	L	L	L	L	L	L	M	L	M
chloroneb	2675-77-6	organochloride	GC	L	L	L	L	L	L	L	L	L	L	H	M	L	L	L	L	L
chlorothalonil	1897-45-6	organochloride	GC	L	H	L	L	M	M	H	H	L	L	H	L	L	L	M	M	H
dieldrin	60-57-1	organochloride	GC	L	L	L	L	L	L	L	L	L	L	L	M	L	L	L	L	M
endrin	72-20-8	organochloride	GC	L	L	L	L	L	L	L	L	L	L	L	M	L	L	L	L	H
heptachlor	76-44-8	organochloride	GC	L	L	M	M	L	L	L	L	M	L	H	H	L	L	H	H	H
heptachlor epoxide	1024-57-3	organochloride	GC	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
hexachlorbenzene	118-74-1	organochloride	GC	L	H	L	L	L	L	L	L	M	L	H	L	L	L	H	H	H
hexachloropentadiene	77-47-4	organochloride	GC	M	H	M	M	M	M	H	H	M	M	H	H	M	L	H	M	H
lindane	58-89-9	organochloride	GC	L	L	L	L	L	L	L	L	L	L	M	M	L	L	L	M	H
methoxychlor	72-43-5	organochloride	GC	L	L	L	L	L	L	L	L	L	L	M	M	M	L	L	L	H
nonachlor (cis)	5103-73-1	organochloride	GC	L	L	L	L	L	L	L	L	L	L	L	L	L	L	M	M	H

Table 3. continued

compound	CAS Registry No.	class	method	FC pH 6.6	FC pH 8.6	MCA pH 6.6	MCA pH 8.6	ClO$_2$ pH 6.6	ClO$_2$ pH 8.6	MnO$_4^-$ pH 6.6	MnO$_4^-$ pH 8.6	H$_2$O$_2$ pH 6.6	H$_2$O$_2$ pH 8.6	O$_3$ pH 6.6	O$_3$ pH 8.6	UV pH 6.6	UV pH 8.6	hydrolysis pH 2	hydrolysis pH 7	hydrolysis pH 12
nonachlor (*trans*)	39765-80-5	organochloride	GC	L	L	L	L	L	L	L	L	L	M	L	L	L	L	M	M	M
chlorpyriphos	2921-88-2	organophosphorus	GC	H	H	L	L	M	M	L	L	L	L	H	M	L	L	L	M	H
diazinon	333-41-5	organophosphorus	GC	H	H	L	L	L	M	L	L	L	L	H	M	L	L	H	L	H
fonofos	944-22-9	organophosphorus	GC	H	H	H	M	H	H	L	L	L	L	H	H	L	L	L	L	H
malathion	121-75-5	organophosphorus	GC	H	H	L	L	L	L	L	L	L	L	M	M	L	L	L	L	H
parathion	298-00-0	organophosphorus	GC	H	H	H	H	H	L	L	L	L	L	H	M	L	L	H	L	H
terbufos	13071-79-9	organophosphorus	GC	H	M	L	L	M	H	M	M	L	L	H	H	L	L	L	H	H
permethrin	52645-53-1	pyrethroid	GC	M	M	L	L	H	M	M	H	L	L	L	L	L	L	H	L	H
fipronil	120068-37-3	pyrazole	LC	H	H	L	L	L	H	H	L	L	L	L	L	L	L	L	L	H
etridiazole	2593-15-9	thiazole	GC	L	L	L	L	L	L	L	L	L	L	L	L	L	L	M	M	H
metribuzin	21087-64-9	triazinone	GC	M	M	L	L	H	H	M	M	L	L	H	L	L	L	M	L	H
atrazine	1912-24-9	triazine	LC	L	L	L	L	L	L	L	L	L	L	L	L	L	L	H	L	L
cyanazine	21725-46-2	triazine	LC	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
prometon	1610-18-0	triazine	LC	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
propazine	139-40-2	triazine	LC	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
simazine	122-34-9	triazine	LC	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
diuron	330-54-1	urea	LC	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
fluometuron	2164-17-2	urea	LC	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L	L
linuron	330-55-2	urea	LC	L	L	L	L	L	L	M	L	L	L	M	M	L	L	L	L	L

pesticides except permethrin and the organochlorides, hexa-chloropentadiene, chlorpyriphos, and diazinon (Table 3). MnO$_4^-$ was highly reactive with aldicarb sulfoxide, aldrin, fipronil, and hexachloropentadiene (Table 3), but recalcitrant with all other compounds except aldicarb, methiocarb, terbofos, permethrin, metribuzin, and linuron (Table 3). Highly reactive pesticides with ozone were distributed across all classes except for ureas, triazines, acidics, a thiazole, and an isoxazole (Table 3).

No compounds were highly reactive with UV$_{254}$ or H$_2$O$_2$ at the typical drinking water treatment exposures used in the study. With UV radiation, only two compounds (methoxychlor and aldrin) showed moderate reactivity at the study dosage. Hydrolysis was at least moderately reactive for 40 of the 62 compounds (65%) studied, with the majority of degradation occurring at acidic and alkaline conditions. A full 48% of the studied pesticides were highly hydrolyzed at the high pH level of 12 (Table 3).

Acid Pesticides. The acidic pesticides (including four aromatic acids and one dicarboxylic acid) were all unreactive and recalcitrant under any of the conditions studied. Thus, the aromatic and dicarboxylic acids studied would not be expected to be significantly transformed under water treatment disinfection conditions.

Literature values for ozone and selected study compounds were available. The ozone exposures ($C \times t$) utilized in the experiments of this screening study were approximately 0.46–0.65 mg·min/L. Even for an exposure of 0.65 mg·min/L, the predicted removal for the lower literature values (1–29.1 M^{-1} s^{-1}) is 0.1–2.3% and consistent with the experimental results. The largest literature value for the ozonation rate constant with 2,4-D (298 M^{-1} s^{-1})[30] corresponds to a 22% "moderate" removal, rather than the "low" (i.e., <20%) removal observed experimentally. The only literature ozonation rate constants found for 2,4,5-TP, dicamba, and picloram, were also observed by Hu et al.;[30] these were 231, 183, and 50 M^{-1} s^{-1}, respectively, and corresponded to predicted removals of 17, 14, and 4%, respectively. Predicted removals for these compounds were consistent with limited literature predictions for direct ozonation of 2,4-D.[30−32]

Amides. Six of the compounds studied were amide (e.g., amide and chloroacetanilide) herbicides. Dimethanamid was shown to be moderately reactive with free chlorine at pH 6.6 (where the hypochlorous acid form is favored) and highly reactive with ozone. At all other conditions, it was relatively unreactive. The other five amide herbicides were largely unreactive with chlorine, monochloramine, chlorine dioxide, hydrogen per-oxide, and UV$_{254}$. All of the compounds (including dimethanamid) were moderately or highly reactive with ozone except propachlor. The primary difference between dimethanamid and the other study compounds is that dimethanamid contains a thienyl ring, whereas the other amides contain an alkyl-substituted benzene ring instead. These findings are consistent with those of Hladik et al.[17] for the compounds alachlor, metolachlor, acetochlor, and dimethanamid. Three of the compounds (alachlor, propachlor, propanil) showed moderate degradation due to hydrolysis after 7 days. These results are also consistent with others. Specifically, Sharma[33] found a half-life of 20 days for alachlor at pH 7. Zheng and Ye[34] found half-lives for acetochlor at pH 4, 7, and 10 of 1400, 2300, and 2300 days, respectively. Kochany and Maguire[35] found <5% degradation for metolachlor at pH 4, 7, and 9 over 100 days.

Benzothiadiazole Herbicide. Bentazone, a thiadiazole herbicide, was highly reactive with ClO$_2$ and O$_3$, but was recalcitrant

to FC, MCA, MnO_4^-, H_2O_2, and UV_{254}. Bentazone was also observed to undergo moderate hydrolysis at pH 2 and 12 and be recalcitrant at neutral pH. An ozone rate constant of 781 M^{-1} s^{-1}, published by Hu et al.,[34] corresponds to a predicted 47% removal, slightly less than the high reactivity observed in this study.

Carbamate Insecticides. A wide range of reactivities were observed for the carbamate insecticides; these were hard to correlate with a subclass. Methiocarb, a phenyl methyl carbamate, was highly reactive with FC, MCA, ClO_2 O_3, and hydrolysis at pH 12 and moderately reactive with MnO_4^- and hydrolysis at pH 2 and 7. The other phenyl methyl carbamate, propoxur, was unreactive to all oxidants and UV (although similarly hydrolyzable).

Three oxime carbamate insecticides (and two degradates) were studied: aldicarb, aldicarb sulfone, aldicarb sulfoxide, methomyl, and oxamyl. Methomyl and oxamyl were generally recalcitrant, except to hydrolysis, and, methomyl was recalcitrant to FC oxidation. Specifically, methomyl was highly reactive to FC, which is consistent with work by Mason,[36] who reported a rate constant of $1.0(10^8)$ M^{-1} s^{-1}, for which the predicted removal was 100% for the typical chlorine exposure of 120 mg·min/L, used in this screening study.

An ozonation rate constant for oxamyl of 620 M^{-1} s^{-1} was published by Yao and Haag,[31] corresponding to a removal of 40% for a 0.65 M^{-1} s^{-1} exposure, consistent with the moderate removals experimentally observed in this study. A paper by Mason et al.,[36] however, found the reaction of methomyl with ozone to be very rapid, which is inconsistent with our findings of low reactivity. No rate constant was cited by Mason et al.,[36] nor were any experimental details provided that would allow further exploration or explanation for the differing results between studies. Further investigation is warranted.

Aldicarb was highly reactive to FC, MCA, ClO_2, O_3, and hydrolysis at pH 12. An ozonation rate constant at pH 7.0 was $4.3(10^5)$ M^{-1} s^{-1}, reported by Yao and Haag,[31] corresponds to a predicted removal of 100%, consistent with the high reactivity observed experimentally in this study. Similarly, a free chlorine rate constant at pH 7.0 was reported to be $1.0(10^5)$ M^{-1} s^{-1} by Mason,[36] thereby predicting the high reactivity (100% removal) observed experimentally.

Waldemer and Tratnyek[37] reported a rate constant of 2.4 M^{-1} s^{-1} for aldicarb and MnO_4^-. For the typical exposure of 75 mg·min/L, used experimentally in this study, the predicted and observed reactives were both low.

Alicarb sulfone, a common degradate, however, was recalcitrant to all oxidants, although it was moderately subject to hydrolysis, even at neutral pH. The degradate, aldicarb sulfoxide, was observed to be highly reactive to MnO_4^- (whereas the parent was not). Aldicarb sulfoxide was also observed to be highly reactive to FC at pH 6.6, but recalcitrant at pH 8.6. Because the acid dissociation constant for aldicarb sulfoxide was approximately 10.9 (SPARC software, ver. 4.2; Hilal et al.[38]), it is hypothesized that speciation of FC to the more reactive hypochlorous acid (predominant at pH 6.6) versus the less reactive hypochlorite ion (predominant at pH 8.6) may be responsible for the observed difference in reactivities.

The thiocarbamate herbicides, EPTC and molinate, were both highly reactive with FC, but generally recalcitrant otherwise (including to hydrolysis) (Table 3). Similarly, the benzofuranyl methylcarbamates, carbofuran and 3-hydroxycarbofuran, were both recalcitrant to all oxidants except for moderate reactivity with ozone, as well as being moderately to highly

hydrolyzable at high pH. Ozonation rate constants of 620 and 387 M^{-1} s^{-1} reported for carbofuran at pH 3.7 and 7.5, respectively,[31,30] correspond to predicted removals of 26 and 40%. These predicted moderate removals are consistent with the experimental results observed.

Dinitroanilines. Two of the compounds studied were dinitroaniline herbicides, pendimethalin and trifluralin. These compounds were unreactive with all oxidants, UV, and hydrolysis, except for ozone. The reason for ozone reactivity is that dinitroanilines contain an amine group, which is susceptible to direct ozone degradation. Both compounds showed low hydrolysis with the exception of trifluralin (with slightly greater than 20% removal). These findings are consistent with the findings of Ramesh and Balasubramanian,[39] who found trifluralin half-lives of 21, 20.7, and 14.8 days for pH 4, 7, and 9, respectively, at 32 °C.

Isoxazole. Another compound studied was the isoxazole (or cyclopropylisoxazole) herbicide isoxaflutole, which proved to be unreactive with all oxidants, UV, and hydrolysis systems studied, except for hydrolysis at pH 12. Beltran et al.[40] found the half-life of isoxaflutole at pH 10.1 to be 0.6 h. Lin et al.[41] oxidized isoxaflutole with free chlorine over an extended period of 60 h and monitored the decrease in concentration of isoxaflutole and the secondary byproduct benzoic acid (BA) (a byproduct of the primary byproduct diketonitrile (DKN). Lin et al. suggested that isoxaflutole is transformed via a two-step process in which it first hydrolyzes to DKN and DKN oxidizes to BA, with the hydrolysis the rate-limiting step. Further research performed by Lerch et al.[42] identified three additional byproducts from DKN oxidation with free chlorine, two of which are known human carcinogens.

Organochlorides. Sixteen of the compounds studied were organochlorine (e.g., cyclodiene, substituted benzene, substituted cyclopentadiene, hexachlorocyclohexane, bridged biphenyl) herbicides, insecticides, and fungicides. Aldrin and hexachloropentadiene showed at least moderate reactivity with free chlorine and permanganate. Heptachlor and hexachloropentadiene showed moderate reactivity with monochloramine, but only slightly above 20% removal. Hexachloropentadiene was the only organochloride to show at least moderate reactivity with chlorine dioxide. Several compounds showed reactivity with hydrogen peroxide, although only hexachloropentadiene was significantly above 20% removal. Aldrin and methoxychlor showed moderate reactivity with UV but only slightly above the threshold of 20% removal. Half of the compounds showed at least moderate reactivity with ozone. Greater reactivity was observed at the higher pH of 8.6 where indirect (rather than direct) ozone reactions may dominate. All compounds except endrin, heptachlor epoxide, and chloroneb showed a propensity to hydrolyze, most notably at alkaline (pH 12) conditions.

Organophosphorus Insecticides. Six of the compounds studied were organophosphorus (organothiophosphate) insecticides. These compounds all showed at least moderate reactivity with free chlorine and ozone. Select compounds were reactive with monochloramine (i.e., fonofos and terbufos), chlorine dioxide (i.e., chlorpyriphos, diazinon, fonofos, and terbufos), and permanganate (i.e., terbufos). The removal of terbufos was only slightly above 20% removal. All of the compounds except malathion degraded significantly at pH 12, whereas diazinon and terbufos were the only pesticides to show significant degradation at pH 2.

The organophosphorus pesticides contain a P=S bond that is highly reactive with FC at pH 6.6 and 8.6. Magara et al.[43] indicated that pesticides with this P=S bond are easily degraded into the primary degradate oxon (P=O) form. These oxon degradates are more toxic than the parent compound.[26] For example, the chlorpyrifos oxon degradate is 1000 times more potent as an anticholinesterase inhibitor and is stable (<50% decrease) at pH 7 over 48 h.[44]

Phthalate. One phthalate (alkyl phthalate) herbicide, dacthal, was studied, and proved to be unreactive with all oxidant/conditions, exhibiting only high reactivity for hydrolysis at pH 12.

Pyrazole. The insecticide fipronil was highly reactive with both FC and MnO_4^- at pH 6.6 and 8.6 and hydrolyzed readily at both low and high pH (Table 3). Fipronil was highly reactive with chlorine dioxide at pH 8.6, but not at pH 6.6 (Table 3). The reason for this is unclear and does not appear to be related to speciation of fipronil based on computational software,[38] which indicates that fipronil does not speciate or ionize with pH.

Triazines and Urea Herbicides. Similarly, the five triazines and three urea herbicides studied were all unreactive and recalcitrant under all conditions studied (with the exception of acid hydrolysis atrazine and cyanazine at pH 2, which normally does not occur in treatment). Overall, these triazine and urea herbicides would not be expected to be transformed in most drinking water treatment plants. Comparison with predicted removals using ozonation rate constants from the literature showed consistent results, that is, very low reactivity for atrazine,[30−32,40] for cyanazine,[30] for simazine,[30,32,40] and for diuron.[45,46] The urea (phenylurea) herbicide linuron was moderately reactive with permanganate and ozone and at other conditions/oxidants indicated low reactivity. The percent removal of linuron with permanganate and ozone was only slightly above 20%.

Thiazole, Triazone, and Pyrethroids. One thiazole (thiadiazole) fungicide, etridiazole, was studied and was reactive only for hydrolysis conditions of pH 2, 7, and 12. One triazinone herbicide, metribuzin, was studied and was at least moderately reactive with free chlorine, chlorine dioxide, permanganate, and ozone. Metribuzin also showed high degradability at pH 2 and 12. One pyrethroid (pyrethroid ester) insecticide, permethrin, was studied and was at least moderately reactive with free chlorine, chlorine dioxide, permanganate, and ozone and hydrolyzed at pH 12.

Overall. Of the 62 pesticides in 15 classes studied, many pesticides were reactive via hydrolysis and/or chlorination and ozonation mechanisms under typical drinking water treatment conditions, with less reactivity exhibited on average for chlorine dioxide, monochloramine, hydrogen peroxide, and UV$_{254}$. The most reactive classes of pesticides were pyrazole and organophosphorous pesticides. Compounds that are degraded all form degradates that may be more or less toxic than the parent itself. Those compounds that did exhibit moderate to high reactivity with select oxidants/conditions warrant further investigation with respect to identification, toxicity, and treatability of the resulting degradates as they relate to drinking water quality and the protection of public health.

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