

# Iron(III) hydroxocomplex - methyl viologen dication system as a prospective tool for determination of hydroxyl radical reaction rate constants with environmental pollutants

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## Research Article

**Keywords:** AOPs, hydroxyl radical, laser flash photolysis, iron hydroxocomplex, methyl viologen dication, reaction rate constants

**Posted Date:** April 27th, 2021

**DOI:** <https://doi.org/10.21203/rs.3.rs-368411/v1>

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**Version of Record:** A version of this preprint was published at Environmental Science and Pollution Research on October 29th, 2021. See the published version at <https://doi.org/10.1007/s11356-021-17166-2>.



23 **ABSTRACT**

24 Reactivity of oxidative species with target pollutants is one of the crucial parameters for  
25 application of any system based on advanced oxidation processes (AOPs). This work presents  
26 new useful approach how to determine the hydroxyl radical reaction rate constants ( $k_{OH}$ ) using  
27 UVA laser flash photolysis technique. Fe(III) hydroxocomplex at pH 3 was applied as a standard  
28 source of hydroxyl radicals and methyl viologen dication ( $MV^{2+}$ ) was used as selective probe for  
29  $\bullet OH$  radical. Application of  $MV^{2+}$  allows to determine  $k_{OH}$  values even for compounds which do  
30 not generate themselves optically detectable transient species in reaction with hydroxyl radicals.  
31 Validity of this approach was tested on a wide range of different persistent pesticides and its  
32 main advantages and drawbacks in comparison with existing steady-state and time-resolved  
33 techniques were discussed.

34 **KEYWORDS:** AOPs, hydroxyl radical, laser flash photolysis, iron hydroxocomplex, methyl  
35 viologen dication, reaction rate constants

36 **DECLARATIONS**

37 *Ethics approval and consent to participate* – “Not applicable”

38 *Consent for publication* -“Not applicable”

39 *Availability of data and materials* -“Not applicable”

40 *Competing interests* - "The authors declare that they have no competing interests"

41 *Funding:* Russian Science Foundation (Grant RSF-NSFC № 21-43-00004) and the National  
42 Natural Science Foundation of China (Grant NSFC-RSF 22061132001)

43 *Authors' contributions:* Y.E. Tyutereva: Investigation, V.P. Grivin: Methodology, Software, J.

44 Xu: Conceptualization, Funding acquisition, F. Wu: Conceptualization, V.F. Plyusnin: Funding

45 acquisition, I.P. Pozdnyakov: Conceptualization, Investigation, Writing - Original Draft, Writing

46 - Review & Editing

47

## 48 INTRODUCTION

49 Advanced oxidation processes based on generation of highly oxidative hydroxyl ( $\bullet\text{OH}$ ) radicals  
50 are very popular nowadays due to increasing contamination of natural waters and necessity to  
51 develop effective and low cost water treatment procedures (Deng and Zhao, 2015; Shen et al.,  
52 2019). As the absorption band of  $\bullet\text{OH}$  radical lies in the deep UV (Buxton et al., 1988) the direct  
53 observation of its reactions with target pollutants is complicated. Usually, unknown hydroxyl  
54 radical reaction rate constant ( $k_{\text{OH}}^{\text{X}}$ ) is determined by competitive method using a substance (S)  
55 with known  $k_{\text{OH}}$  value as a standard (Haag and Yao, 1992, Orellana-García et al., 2015, Sánchez-  
56 Polo et al., 2013). The main advantage of aforesaid approach is the possibility to use steady-state  
57 (photo)chemical methods of generation of  $\bullet\text{OH}$  radical and widespread and convenient HPLC  
58 technique for calculation of  $k_{\text{OH}}^{\text{X}}$  value. However, this approach has some serious drawbacks as  
59 follows:

- 60 1) This is relative method giving  $k_{\text{OH}}^{\text{X}}/k_{\text{OH}}^{\text{S}}$  ratio in result, so standard with very well  
61 determined  $k_{\text{OH}}^{\text{S}}$  value has to be used.
- 62 2) If photochemical excitation is used for  $\bullet\text{OH}$  radical generation, neither X nor S should  
63 exhibit good absorption and/or own photochemical activity under excitation light.
- 64 3) If there are reactions between secondary organic radicals and initial compounds X and S,  
65 the determination of  $k_{\text{OH}}^{\text{X}}$  using this method will give an incorrect result.

66 Less popular, but more straightforward approach is based on using a time-resolved method (laser  
67 flash photolysis (LFP) or pulse radiolysis (PR), namely), which allows direct optical registration  
68 of  $\bullet\text{OH}$  radical reaction with target compound (Peller et al., 2005; Rafqah et al., 2004; Terzian et  
69 al., 1995; Zona et al., 2012). The main advantage of this approach that it is absolute method  
70 which allows direct calculation of  $k_{\text{OH}}^{\text{X}}$  values. However, it also has some drawbacks as follows:

- 71 1) Both LFP and PR techniques are less common and more sophisticated methods in  
72 comparison with ordinary HPLC.

73 2) In LFP method a photochemical system with high quantum yield of hydroxyl radical  
74 generation is needed and X should not exhibit good absorption and/or own  
75 photochemical activity under excitation light.

76 3) If  $\bullet\text{OH}$  adduct with X molecule exhibits low absorption in registration range of LFP or  
77 PR setup or its absorption is borrowed by intensive absorption of initial compounds, the  
78 calculation of  $k_{\text{OH}}^{\text{X}}$  will be very complicated or even impossible.

79 Last two drawbacks could be overcome by addition of another hydroxyl radical probe which do  
80 not absorb at excitation wavelength, reacts readily with hydroxyl radical and produce an  
81 intermediate with good absorption in convenient optical range (Catastini et al., 2004). In this  
82 work we developing this approach using Fe(III) hydroxocomplex as well-recommended  
83 photolytic source of hydroxyl radical and methyl viologen dication as a selective probe for this  
84 active species.

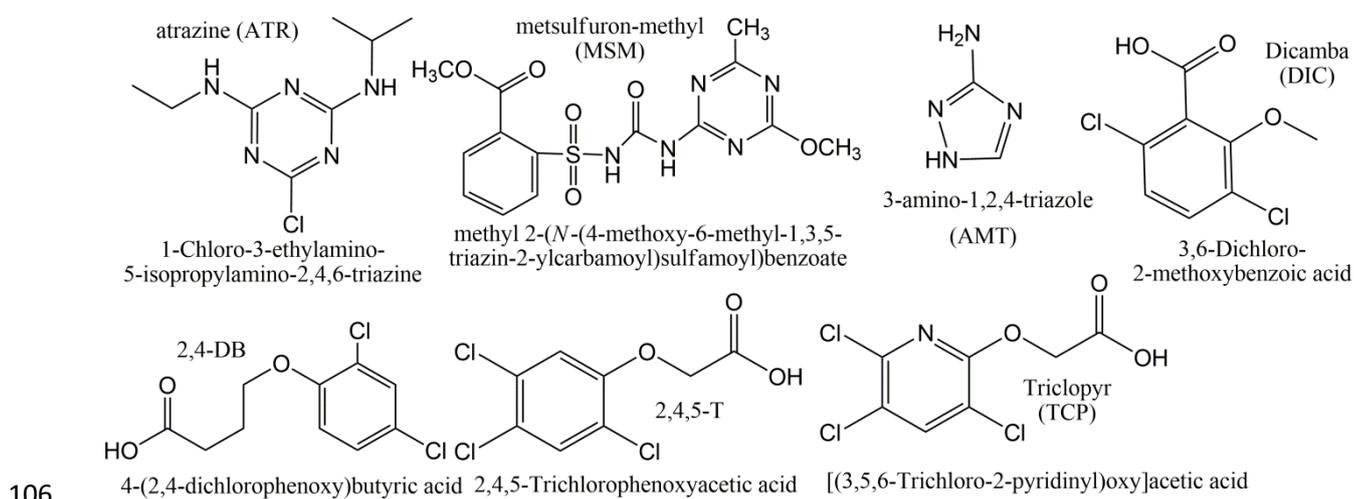
## 85 **EXPERIMENTAL**

86 All chemicals used in the study were of analytical reagent grade or higher purity and were used  
87 without further purification. Milli-Q water was used in all photochemical experiments. The  
88 initial pH of solutions was adjusted to  $\sim 3$  by chemically pure perchloric acid and was controlled  
89 by the Anion-4100 ionometer (Infrapak-Analit, Russia). Optical spectra were recorded using  
90 Agilent 8453 spectrophotometer (Agilent Technologies, USA).

91 Time-resolved experiments were performed using a laser flash photolysis (LFP) setup described  
92 in details elsewhere (Pozdnyakov et al., 2006). Briefly, a tunable LS-2137U laser (Lotis,  
93 Belarus) with an excitation wavelength of 355 nm was used as excitation source with pulse  
94 duration of about 6 ns, and pulse energy from 1 to 15 mJ. Quartz cells with an optical path length  
95 of 1 cm and a total volume of 3 ml at normal oxygen content in solutions were applied.

## 96 **RESULTS AND DISCUSSION**

97 The set of organic pesticides used in this study as typical environmental contaminants is  
 98 presented in Fig 1. It worth to note, that all of these compounds exhibit no absorption at 355 nm,  
 99 are stable in the presence of Fe(III) ions and do not complex with them. It was demonstrated by  
 100 coincidence of sum of absorption spectra of individual species with spectrum of the mixture and  
 101 stability of the latter during characteristic times of LFP experiments. It is also assumed that X-  
 102 •OH adducts exhibit negligible absorption at wavelengths higher than 400 nm. Such situation is  
 103 typical for X-•OH adducts formed upon hydroxyl radical attack to benzene ring (Buxton et al.,  
 104 1988; Terzian et al., 1995, Zona et al., 2002) and coincide with known literature data for target  
 105 compounds (Table 1).



107 **Figure 1.** The structural formulae of organic pesticides used in this study

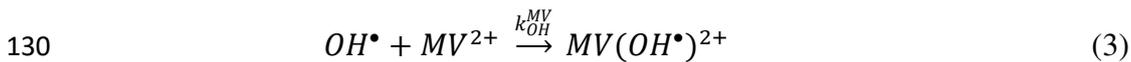
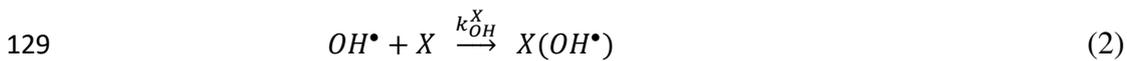
108 The elementary reactions of •OH radicals with target pollutants were studied with efficient  
 109 sensitizer of these radicals, Fe(OH)<sup>2+</sup> hydroxocomplex (Benkelberg et al., 1995; Lee and Yoon,  
 110 2004; Pozdnyakov et al., 2000). In our LFP experiments the concentration of Fe(III) perchlorate  
 111 was fixed as 600 μM at pH 2.9 In these conditions the FeOH<sup>2+</sup> hydroxocomplex was a main  
 112 form of Fe(III) in solution (about 80%) and a sole photoactive species with absorption of about  
 113 50% of UV light quanta.



115 As a selective probe for  $\bullet\text{OH}$  radical  $\text{MV}^{2+}$  was proposed which has several advantages as  
 116 follows:

- 117 1) Has no own absorption at wavelength higher than 310 nm and does not interact or  
 118 oxidized by Fe(III) ions in acid media.
- 119 2) Reacts readily with hydroxyl radical with rate constant  $(2.5 \pm 0.2) \times 10^8 \text{ M}^{-1}\text{s}^{-1}$  (Solar et  
 120 all., 1985; Zhang et al., 2008)
- 121 3) Produce  $\text{MV}(\bullet\text{OH})^{2+}$  intermediate with good absorption in convenient optical range ( $\lambda_{\text{max}}$   
 122 = 470 nm,  $\epsilon_{\text{max}} = 16000 \pm 700 \text{ M}^{-1}\text{cm}^{-1}$ , Solar et al., 1985; Zhang et al., 2008) where  
 123 does not absorb nor Fe(III) hydroxocomplex, not adducts of  $\bullet\text{OH}$  radical with target  
 124 compounds.

125 In condition of our LFP experiments typical  $\bullet\text{OH}$  radical concentration is about 1  $\mu\text{M}$  which is  
 126 much less then concentration of both  $\text{MV}^{2+}$  (240  $\mu\text{M}$ ) and target compounds (25 – 500  $\mu\text{M}$ )  
 127 used in this study. It allows taking into account only reactions of  $\bullet\text{OH}$  radical with aforesaid  
 128 compounds and use psevdo first order approximation in solving of the following kinetic scheme:



$$132 \quad \frac{d[\text{OH}\bullet]}{dt} = -(k_{\text{OH}}^{\text{X}}[\text{X}]_0 + k_{\text{OH}}^{\text{MV}}[\text{MV}^{2+}]_0)[\text{OH}\bullet] \quad (5)$$

$$133 \quad \frac{d[\text{MV}(\text{OH}\bullet)^{2+}]}{dt} = k_{\text{OH}}^{\text{MV}}[\text{MV}^{2+}][\text{OH}\bullet] - k_d[\text{MV}(\text{OH}\bullet)^{2+}] \quad (6)$$

134 Where  $k_d$  is the observed rate constant of  $\text{MV}(\bullet\text{OH})^{2+}$  adduct decay. It worth to note that  
 135 according to Solar et al., the main pathway of  $\text{MV}(\bullet\text{OH})^{2+}$  disappearance in aqueous solutions is  
 136 disproportionation with the rate constant,  $2k_{\text{dis}} = (1.3 \pm 0.2) \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ . However, due to very  
 137 low concentration of  $\text{MV}(\bullet\text{OH})^{2+}$  adduct we can successfully use first-order reaction (4) to

138 describe the decay of this species in our time window (Fig. 2). Solution of kinetic scheme (5-6)  
 139 gives the dependence of  $MV(\bullet OH)^{2+}$  adduct concentration on time:

$$140 \quad [MV(OH\bullet)^{2+}] = \frac{k_{OH}^{MV}[MV^{2+}]_0[OH\bullet]_0}{(k_{obs}-k_d)} [e^{(-k_d t)} - e^{(-k_{obs} t)}] \quad (7)$$

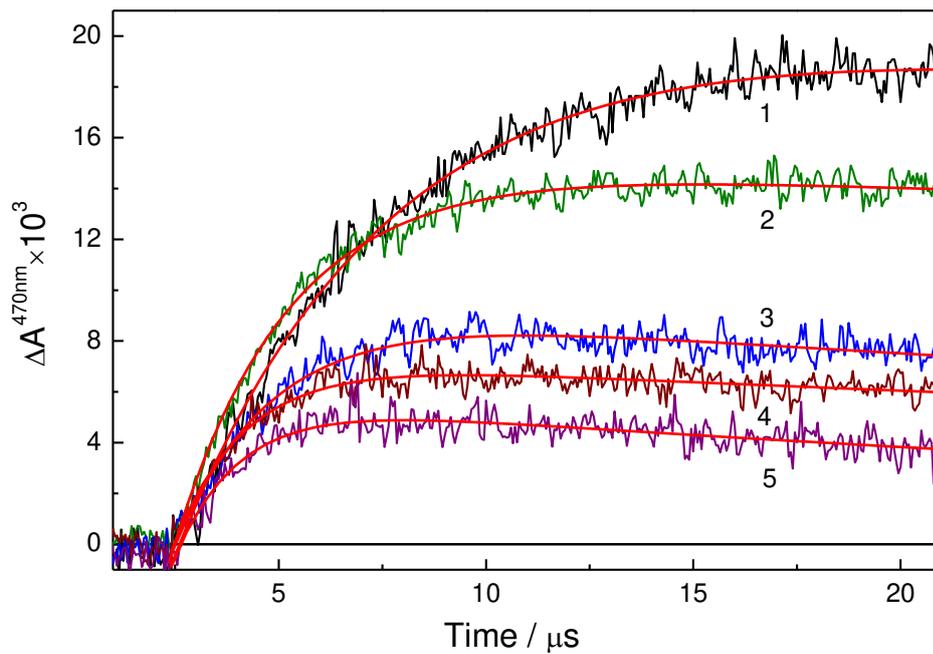
141 Where

$$142 \quad k_{obs} = k_{OH}^{MV}[MV^{2+}]_0 + k_{OH}^X[X]_0 \quad (8)$$

143 Taking into account that only  $MV(\bullet OH)^{2+}$  adduct exhibits transient absorption at 470 nm  
 144 ( $\Delta A^{470nm}(t)$ ) one can obtain the following equation for changing of this parameter with time:

$$145 \quad \Delta A^{470nm}(t) = \varepsilon_{max} \frac{k_{OH}^{MV}[MV^{2+}]_0[OH\bullet]_0}{(k_{obs}-k_d)} [e^{(-k_d t)} - e^{(-k_{obs} t)}] = A[e^{(-k_d t)} - e^{(-k_{obs} t)}] \quad (9)$$

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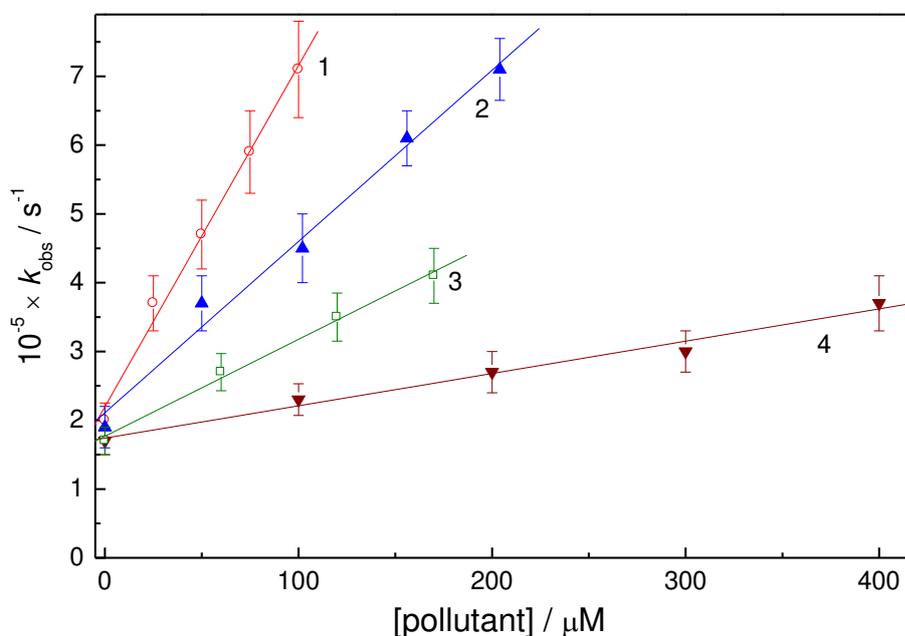


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148 **Figure 2.** Kinetic curves of transient absorption of  $MV(\bullet OH)^{2+}$  adduct at 470 nm in presence of 0  
 149 (1), 25 (2), 50 (3), 75 (4) and 100 (5)  $\mu M$  of 2,4-DB. Each curve was obtained by averaging of  
 150 20-30 independent laser flashes, excitation energy was 5.6 mJ/pulse. Smooth curves are the best  
 151 fits by eq. 9.

152

153 Evolution of transient absorption of MV( $\bullet$ OH) $^{2+}$  adduct at 470 nm in the presence of different  
154 concentration of 2,4-DB herbicide is shown at Figure 2. Similar results were obtained for all  
155 other target compounds used in the study. It worth to note that amplitude of the signal at 470 nm  
156 is gradually decrease with increasing of 2,4-DB concentration due to competition between the  
157 herbicide and MV $^{2+}$  for  $\bullet$ OH radicals (eq. 9). However in all cases signal to noise ratio is high  
158 enough to determine  $k_{\text{obs}}$  value with about 10-15% precision. Very good fit was obtained for all  
159 concentration of 2,4-DB as well as for other compounds (Fig. 3) which proves validity of  
160 simplified kinetic scheme (5-6) and allows to calculate  $k_{\text{OH}}^X$  values for studied pesticides (Table  
161 1).



162

163 **Figure 3.** The dependence of  $k_{\text{obs}}$  calculated by eq. 9 from initial concentration of 2,4-DB (1),  
164 MSM (2), TCP (3) and AMT (4). Straight lines are the best fits by eq. 8.

165 Analysis of data presenting in Table 1 allows to conclude that our approach gives the  $k_{\text{OH}}^X$   
166 values which are well coincides with result obtaining by both steady-state (stationary photolysis,  
167 ozonation) and time-resolved (LPF, PR) methods. It worth to note that  $k_{\text{OH}}^X$  values are  
168 practically independent on pH for the studied compounds. It could be explained by the fact that  
169 studied herbicides (for exception of AMT, ATR and DIC) do not contain an acid/base substituent

170 directly attached to aromatic  $\pi$ -system. For this reason deprotonation of an aliphatic substituent  
171 does not change greatly red-ox properties of a target molecule and its reactivity towards  
172 hydroxyl radical. This is clearly seen in comparison of  $k_{OH^X}$  values for 2,4-DB, 2,4,5-T and TCP  
173 which are practically the same for both neutral and anionic form of the herbicide. In a case of  
174 ATR at all pH higher than 2.5 these compound exists mainly in neutral form ( $pK_a = 1.6$ ), so  $k_{OH^X}$   
175 values for this compound is not affected by pH (Table 1). Similar situation is expected for DIC  
176 ( $pK_a = 1.9$ ) which exist as monoanion in environmentally relevant pH range.

177 For AMT which contains protonated amino group directly attached to the triazole  $\pi$ -system  $k_{OH^X}$   
178 increase about 1.6 times for neutral form in comparison with cationic one (Table 1). So we can  
179 conclude that for aromatic amines, phenols and similar compounds with  $pK_a$  values higher than 3  
180  $k_{OH^X}$  values obtained by our approach could be used only as tentative estimates of the reactivity  
181 of the compounds towards hydroxyl radical at higher pH. However, our approach allows to  
182 measure  $k_{OH^X}$  values for a set of target compounds (from two to four) for a day due to high  
183 analytical signal of  $MV(\cdot OH)^{2+}$  adduct at selected registration wavelength (470 nm). It is not a  
184 case of general approach using LFP or PR techniques where one first needs to find the  
185 absorption maximum of unknown adduct of  $\cdot OH$  radical with studied contaminant and this is  
186 limiting time-consuming step. In a case of application of steady-state techniques one need to  
187 spend a time for finding a proper competing standard and for time-consuming HPLC  
188 measurements.

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Compound (pK <sub>a</sub> )	pH	$k_{OH^X} \times 10^{-9}$ M <sup>-1</sup> s <sup>-1</sup>	$\lambda_{max}(X\text{-}\bullet\text{OH})$ nm	Method <sup>a</sup>	reference
AMT (4.14)	3.4	1.5	< 300	LFP	Catastini et al., 2004
	3.0	0.36 ± 0.02	-	SSP	Orellana-García et al., 2015
	7.0	0.59 ± 0.03	-	SSP	Orellana-García et al., 2015
	2.9	0.47 ± 0.04	-	LFP	This work
ATR (1.6)	3.0	2.9	-	SSP	Orellana-García et al., 2015
	7.0	2.7	-	SSP	Orellana-García et al., 2015
	3.6	2.6 ± 0.4	-	SSP	Haag and Yao, 1992
	2.9	3.5 ± 0.6	-	LFP	This work
2,4-DB (2.6)	2.5	5.2	310	PR	Peller et al., 2005 <sup>b</sup>
	9.0	6.6	310	PR	Zona et al., 2002 <sup>b</sup>
	3.0	~7.0	315	LFP	Pozdnyakov et al., 2016
	2.9	5.0 ± 0.3	-	LFP	This work
DIC (1.9)	2.9	3.2 ± 0.3	-	LFP	This work
MSM (3.75)	3.4	3.5	355	LFP	Rafqah et al., 2004
	2.9	2.5 ± 0.2	-	LFP	This work
2,4,5-T (2.7)	8.5	6.4	320	PR	Zona et al., 2012
	2.9	6.3 ± 0.5	-	LFP	This work
TCP (2.7)	7.0	1.7	-	Ozonation	Solís 2014
	2.9	1.4 ± 0.3	-	LFP	This work

195 <sup>a</sup>SSP, LFP and PR stands for steady-state photolysis, laser flash photolysis and pulse radiolysis,  
196 accordingly; <sup>b</sup>data for 2,4-D (2,4-dichlorophenoxyacetic acid) a close analogue of 2,4-DB was  
197 taken.

198 **CONCLUSIONS**

199 LPF of Fe(III) hydroxocomplex - MV<sup>2+</sup> system at pH 3 could be successfully used to determine  
200  $k_{OH}$  values for a wide range of different persistent pesticides. Validity of this approach was  
201 proven on by comparison of obtained  $k_{OH}$  values with literature ones found by another  
202 approaches. The main advantages of proposed system in comparison with existing popular  
203 competitive steady state approaches or direct LFP with target molecule are as follows:

- 204 1) Absolute method allowing direct measurement of  $k_{OH}$  value in opposite to competitive  
205 steady state approaches.
- 206 2) MV( $\bullet$ OH)<sup>2+</sup> adduct absorption spectrum does not overlap with spectra of  $\bullet$ OH adducts  
207 with typical environmental contaminants.
- 208 3) “One-wavelength registration” method, allowing to avoid time-consuming determination  
209 of transient absorption spectrum of  $\bullet$ OH adduct with a studied environmental  
210 contaminant.
- 211 4)  $k_{OH}$  values could be obtained with good experimental precision (c.a. 10-15%) due to high  
212 absorption of MV( $\bullet$ OH)<sup>2+</sup> adduct in convenient optical range ( $\lambda_{max} = 470$  nm,  $\epsilon_{max} =$   
213  $16000 \pm 700$  M<sup>-1</sup>cm<sup>-1</sup>).
- 214 5) The method could be applied for compounds which do not generate themselves optically  
215 detectable transient species in reaction with hydroxyl radicals.

216 However, some limitations of aforesaid approach also should be stressed:

- 217 1) The method should not be applied for compounds which generate X( $\bullet$ OH)<sup>2+</sup> adducts with  
218 good absorption at 470 nm. In this case direct measurement of observed rate constant of  
219 formation of transient absorption of X- $\bullet$ OH adduct in the maximum of its absorption is  
220 recommended.

221 2) For aromatic amines, phenols and similar compounds with  $pK_a$  values higher than three  $k_{OH}^X$   
222 values obtained by our approach could be used only as tentative estimates of the reactivity of the  
223 compounds towards hydroxyl radical at higher pH.

224 We believed that current approach will be successfully used in the studies devoted to application  
225 of AOPs based on hydroxyl radical generation for determination of  $k_{OH}$  values for target  
226 environmental contaminants.

## 227 **ACKNOWLEDGEMENTS**

228 The financial support of the Russian Science Foundation (Grant RSF-NSFC № 21-43-00004)  
229 and the National Natural Science Foundation of China (Grant NSFC-RSF 22061132001) is  
230 gratefully acknowledged.

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# Figures

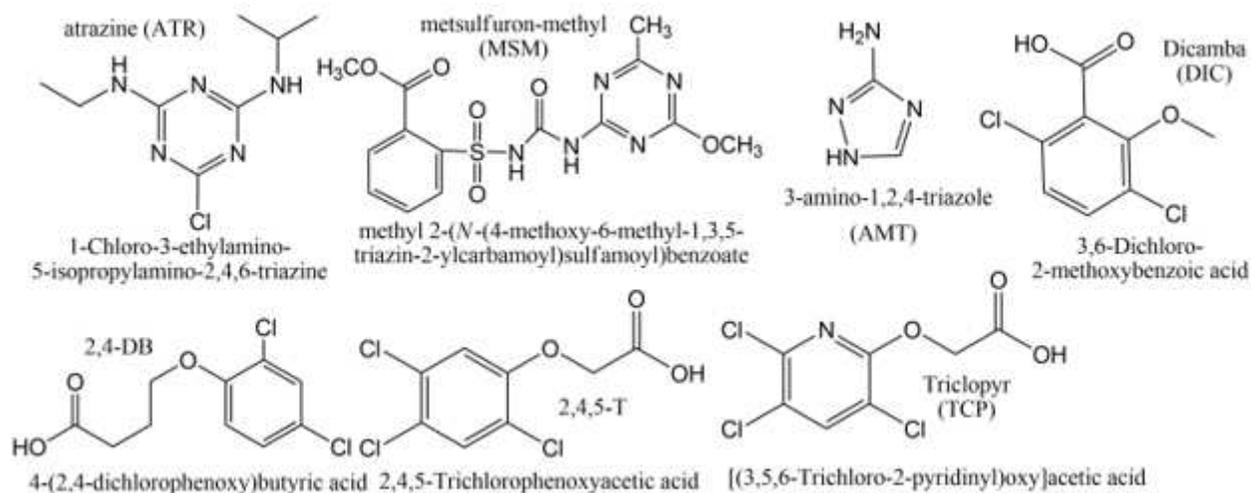


Figure 1

The structural formulae of organic pesticides used in this study

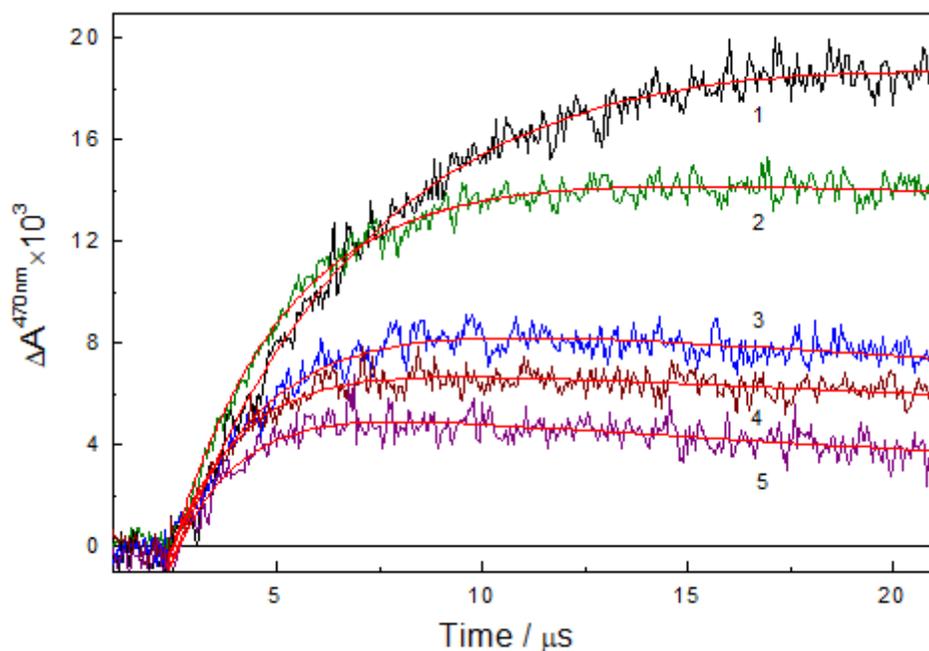
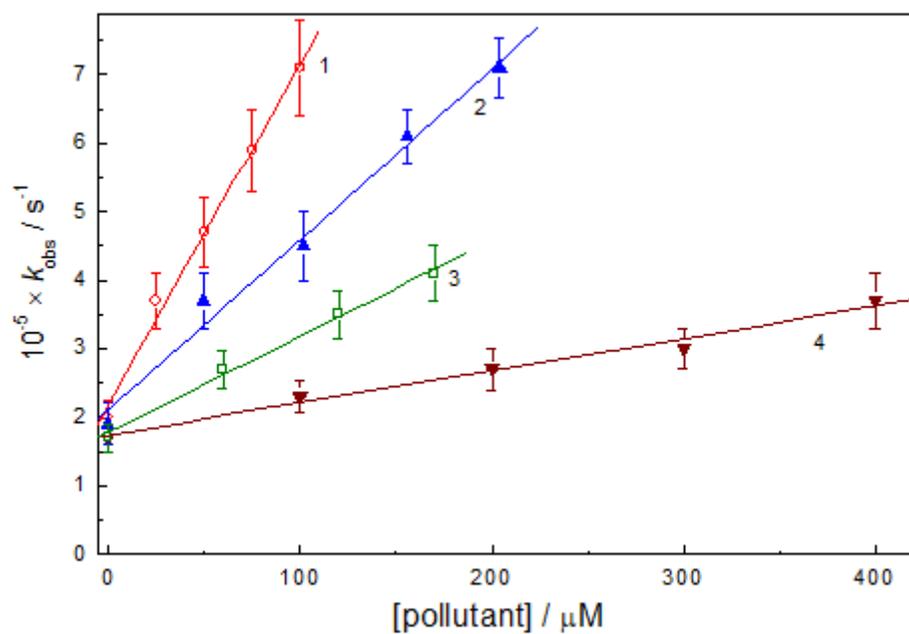


Figure 2

Kinetic curves of transient absorption of MV( $\cdot$ OH) $_2^+$  adduct at 470 nm in presence of 0 (1), 25 (2), 50 (3), 75 (4) and 100 (5)  $\mu$ M of 2,4-DB. Each curve was obtained by averaging of 20-30 independent laser flashes, excitation energy was 5.6 mJ/pulse. Smooth curves are the best fits by eq. 9.



**Figure 3**

The dependence of  $k_{\text{obs}}$  calculated by eq. 9 from initial concentration of 2,4-DB (1), MSM (2), TCP (3) and AMT (4). Straight lines are the best fits by eq. 8.