Photochemistry of *N*-(Phosphonomethyl)glycine in the Presence of Ferric Ions

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Ferric complex $[Fe(gly)_2]^{3-}$ (gly^{3-} = anion of *N*-(phosphonomethyl)glycine) undergoes a photoredox transformation when being irradiated with UV radiation both in aqueous and methanolic media. Photoreduction of Fe(III) to Fe(II), occurring in deoxygenated systems, is accompanied by decomposition of the coordinated ligand. As the products of this photodecomposition, formaldehyde, ammonia, and new phosphorus-containing species were identified in aqueous media. Along with the photoinduced oxidation of the ligand, molecules of solvent are oxidized in methanolic media as well. In the presence of oxygen no net Fe(III) reduction is observed. Photochemical degradation of *N*-(phosphonomethyl)glycine was monitored using ^{31}P NMR and electronic absorption spectroscopy. Attempts to rationalize the spectral changes and the mechanism of the photochemical processes are involved.

N-(Phosphonomethyl)glycine, $HO_2C—CH_2—NH—CH_2—PO_3H_2$, known as glyphosate, is the active substance of the Monsanto herbicide Roundup, sales of which have reached more than 10^9 $ per year [1]. Commercial herbicides usually contain the isopropylamine salt of glyphosate. One of the most remarkable characteristics of glyphosate lies in its change from a herbicide to a fertilizer, which is caused by its gradual decomposition to nontoxic products CO_2, H_3PO_4, and NH_3 in soil. Another remarkable property of glyphosate is the short time of its persistence in soil.

Glyphosate, depending on the degree of its deprotonation, can coordinate as mono-, bi- or tridentate ligand, hence it can form a series of complexes with metal cations. In principle, trianionic form of glyphosate gly^{3-} can coordinate through an oxygen atom of the carboxylic group, an oxygen atom of the phosphonate group, and the nitrogen atom. Potentiometric titration has provided data for identifying 1:1 and 1:2 complexes in solutions containing kinetically labile metal ions and glyphosate [2]. In the case of complexes with an inert central atom, isomers having different structures can be distinguished. An existence of the isomers can be a consequence of the different denticity of coordinated glyphosate, of the different degree of its deprotonation which depends predominantly on pH, and of the symmetry of the ligand or the complex. For example, 16 isomers of the complex $[Co(gly)_2]^{3-}$ have recently been described [3]. Taking into account the complexes with glyphosate coordinated as a bidentate or a monodentate ligand, a number of potential isomers is even higher.

It has been found that glyphosate has deactivated in soil and has not acted as a herbicide at certain conditions. It has also been supposed that such a decrease in glyphosate activity might be attributed, along with its degradation, to the complex formation processes with cations present in soil [1]. Of the metal cations contained in soil, iron(III) seems to be a good candidate for such a complex formation. Bound in a complex, glyphosate is not able to penetrate into plants and "fulfil its duty" Another reason of the glyphosate deactivation in the presence of metal ions can lie in the photoredox processes of the complexes having been formed. Glyphosate itself does not absorb solar radiation, its transition metal complexes, however, do it. Since the ability of Fe(III) complexes to undergo effective photoredox decomposition is a well-known fact [4], in the framework of our investigation of the photochemical properties of Fe(III) complexes with commercially interesting ligands, we have focused our attention to the photoredox properties of Fe(III) complexes containing glyphosate in their primary coordination sphere. The results obtained are presented in this paper.

EXPERIMENTAL

Glyphosate as free acid H_3gly was kindly gifted by Monsanto, it was twice recrystallized from water before use and melting point was determined to be 200 °C. Distilled water and anhydrous methanol (Aldrich, anal. grade) were used as solvents. The spin traps 5,5-dimethyl-1-pyrrolidine *N*-oxide (DMPO) and nitrosodurene (ND) (Sigma) were used without further purification. The other chemicals were from Lachema, all being of anal. grade and used as received.

The irradiated solutions were prepared by dissolving solid glyphosate H_3gly, $Fe(NO_3)_3 \cdot 9H_2O$, and $NaOCH_3$ in methanol so as to obtain solutions with initial $c(Fe^{III}) = 1.6 \times 10^{-4}$ mol dm^{-3}, $c(Fe^{III})$: $c(H_3gly)$: $c(NaOCH_3) = 1:3:2$. In aqueous solutions, NaOH was used instead of $NaOCH_3$. Steady-state photolysis was performed in a three-chambered temperature-controlled quartz photoreactor equipped with a medium-pressure Hg-lamp (Tesla RVK, 125 W, radiation monochromatized by solution filters [5]) or a low-pressure Hg-lamp (Germicidal Lamp G8T5). The volume of irradiated solutions in the photoreactors was 120 cm^3 Solutions were irradiated both in the presence and in the absence of oxygen (in the latter case the solutions were deoxygenated by bubbling with argon for 30 min before and during the irradiation). The wavelength of the incident radiation was 254 nm or 313 nm, its quantum intensity, determined by a ferrioxalate actinometer was of the order of 10^{18} s^{-1} cm^{-2}

Time-resolved absorption spectra were obtained using a Spectron SL-402 Nd:YAG laser ($\lambda_{irr} = 266$ nm, pulse energy = 10—20 mJ, a width of pulse ≈ 15 ns) connected with Applied Photophysics KS-347 kinetic spectrometer and Philips PM3320/A digitizing storage oscilloscope. In flash photolytic studies, solutions were irradiated directly in quartz cuvettes.

The photoreduction of Fe(III) to Fe(II) was followed by plotting $c(Fe^{II})$ *vs.* irradiation time. The content of the formed Fe(II) was determined on the basis of known spectral properties of the complex $[Fe(phen)_3]^{2+}$ Formaldehyde was determined as 3,5-diacetyl-1,4-dihydrolutidine (DADL), ammonia was identified in irradiated solutions by Nessler's reagent. Details on the evaluation of photochemical data and the used analytical procedures are described elsewhere [5].

Radical formation was followed using spin traps 5,5-dimethyl-1-pyrrolidine *N*-oxide and nitrosodurene added to a deoxygenated methanolic solution of the complex $[Fe(gly)_2]^{3-}$ irradiated with polychromatic radiation emitted by a 250 W medium-pressure Hg-lamp (Applied Photophysics) directly in the rectangular cavity of an EPR equipment. EPR spectra simulation was performed using a standard Bruker program.

The changes in the total amount of glyphosate in the irradiated systems were followed by HPLC and ^{31}P NMR. HPLC measurements were performed on an HPLC apparatus equipped with a high-pressure pump HPP 5001, a UV detector LCD 2040 or an electrochemical microdetector EMD 10 with polarization voltage ranged from 0.8 V to 1.2 V, a line recorder TZ 4620, and a computing integrator CI 100 (Laboratory Instruments, Prague). NMR spectra were scanned on a Varian VXR spectrometer with the resonance frequency of 299.942 MHz and 121.421 MHz for ^1H and ^{31}P, respectively. As an internal standard, a solution of Na_2HPO_4 with $c(Na_2HPO_4) = 4.0 \times 10^{-2}$ mol dm^{-3} was used. Iron was removed as $Fe_2O_3 \cdot nH_2O$ after treating the solutions with an excess of aqueous KOH solution. Electronic absorption spectra were measured on a Specord M-40 spectrometer (Zeiss, Jena). EPR spectra were recorded on a Bruker 200D spectrometer.

RESULTS AND DISCUSSION

Measurements of the electronic absorption spectra of glyphosate in water and methanol at different pH documented that any form of the compound was radiation transparent in the region of $\lambda = 220$—800 nm.

Solutions of the complex $[Fe^{III}(gly)_2]^{3-}$ were prepared according to [2]. Electronic absorption spectrum of the complex (curve *i* in Fig. 1) consists of a structured band with shoulders located at 250 nm ($\varepsilon_{250} = 7.800$ mol^{-1} dm^3 cm^{-1}) and 310 nm ($\varepsilon_{310} = 4.400$ mol^{-1} dm^3 cm^{-1}). In the absence of visible or ultraviolet radiation, solution spectra of the complex $[Fe^{III}(gly)_2]^{3-}$ both in water and in methanol do not undergo any change and no spontaneous reduction of Fe(III) to Fe(II) occurs.

Flash photolysis at 266 nm reveals that the absorption of a photon by the complex leads in the first stage to a bleaching in the whole UV region followed by a slow (in the time scale of seconds) reappearance of the spectra. The effect, monitored at 300 nm is shown in the inset of Fig. 1.

The nature of the spectral changes during continuous irradiation of oxygen-containing systems at 254 nm or 313 nm can be seen in Fig. 1. The time evolution of the spectra can be divided into two parts. In the initial period of irradiation the absorbance increases in the whole region (the higher intensity of the incident radiation and the shorter its wavelength, the higher is the rate of the spectral changes). The increase in absorbance is accompanied by small changes in the spectral curve. A new peak centred at 261 nm is formed ($\varepsilon_{261} = 15.000$ mol^{-1} dm^3 cm^{-1}) and new poorly resolved shoulders appear (curve *m* in Fig. 1). When interrupting the irradiation, the spectrum slowly reverts to the initial one. Prolonged irradiation causes a decrease of the absorbance (curve *f* in Fig. 1). In the presence of oxygen, no significant net reduction of Fe(III) to Fe(II) was observed.

Irradiation of both aqueous and methanolic solutions of the complex $[Fe^{III}(gly)_2]^{3-}$ in the absence of

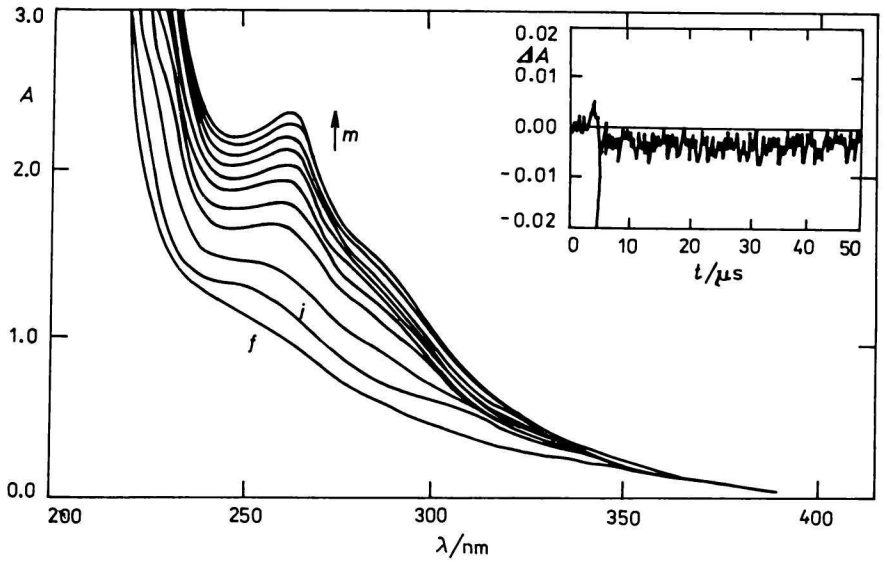

Fig. 1. Time evolution of the absorption spectra of 1.6×10^{-4} mol dm^{-3} $[Fe(gly)_2]^{3-}$ irradiated in methanol at 254 nm in the presence of oxygen; t_{irr} = 0 (*i*), 10 min (*m*), 60 min (*f*). Inset: time dependence of absorbance monitored at 300 nm following a 266 nm flash.

oxygen leads to a linear time evolution of $c(Fe^{II})$. In methanolic solutions the formation of Fe(II) is accompanied by a simultaneous formaldehyde formation. Based on the spectral characteristics [5] of DADL used in CH_2O determination (ε_{410}(DADL) = 8.000 mol^{-1} dm^3 cm^{-1}) and those of $[Fe(phen)_3]^{2+}$ used in Fe(II) determination ($\varepsilon_{510}([Fe(phen)_3]^{2+}) = 11.200$ mol^{-1} dm^3 cm^{-1}) the observed time dependences of absorbance were transformed into time dependences of the molar amount of photochemically formed CH_2O and Fe(II)

$$\mathrm{d}n(CH_2O)/\mathrm{d}t = (\mathrm{d}A_{410}(\mathrm{DADL})/\mathrm{d}t)\,(V/(\varepsilon_{410}(\mathrm{DADL})\ l) \quad (1)$$

$$\mathrm{d}n(Fe^{II})/\mathrm{d}t = (\mathrm{d}A_{510}([Fe(phen)_3]^{2+})/\mathrm{d}t\,(V/\varepsilon_{510}([Fe(phen)_3]^{2+})\ l) \quad (2)$$

where l is the path length of cell. Time evolutions of the molar amount of the photochemically formed Fe(II) and CH_2O in the system with the initial concentration $c([Fe^{III}(gly)_2]^{3-}) = 1.60 \times 10^{-4}$ mol dm^{-3}, irradiated at 254 nm ($I_{abs} = 1.23 \times 10^{-6}\ N_A\ h\nu$ s^{-1}) are shown in Fig. 2. Computer treatment of the data led to the values of $\mathrm{d}n(CH_2O)/\mathrm{d}t = 1.21 \times 10^{-8}$ mol s^{-1} and $\mathrm{d}n(Fe^{II})/\mathrm{d}t = 6.17 \times 10^{-9}$ mol s^{-1} The mole ratio calculated of the above values is $n(Fe^{II}):n(CH_2O) = 1:1.96$. Overall quantum yields ϕ of CH_2O and Fe(II) formation in this system (Table 1), calculated according to

$$\phi = \mathrm{d}n/\mathrm{d}I_{abs} \quad (3)$$

where $\mathrm{d}n$ relates to a product and $\mathrm{d}I_{abs}$ to the reactant, both the quantities relating to the unit time, are

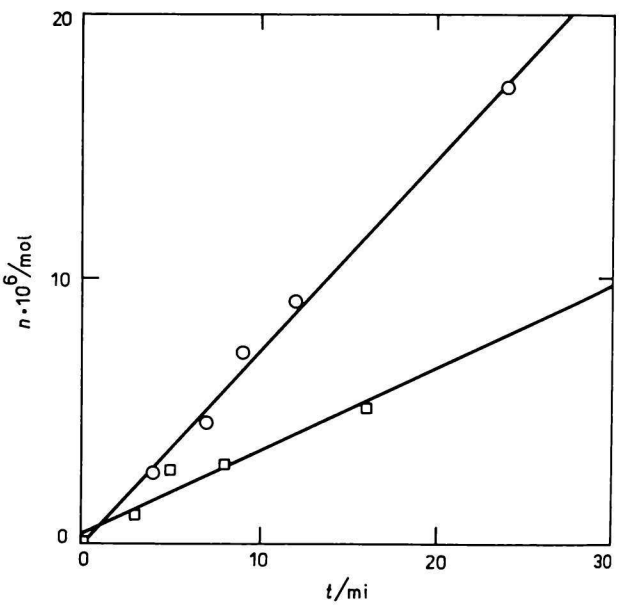

Fig. 2. Plots of the molar amount of Fe(II) (□) and CH_2O (○) formed during a 254 nm photolysis of deoxygenated methanolic 1.6×10^{-4} mol dm^{-3} $[Fe(gly)_2]^{3-}$

as follows: $\phi(CH_2O) = 1.02 \times 10^{-2}$, $\phi(Fe^{II}) = 5.20 \times 10^{-3}$

It follows from the stoichiometry, written for the sake of simplicity as

$$2\ Fe^{3+} + CH_3OH \xrightarrow{h\nu} 2\ Fe^{2+} + 2\ H^+ + CH_2O \quad (A)$$

that irradiation of methanolic solutions containing Fe(III) complexes gives rise to the mole ratio of $c(Fe^{II}):c(CH_2O) = 2:1$ in cases where the only fi-

Table 1. Overall Quantum Yields of Fe(II) Formation, $\phi(\lambda_{irr}/nm)$, for the Complex $[Fe(gly)_2]^{3-}$ Irradiated in Deoxygenated Aqueous or Methanolic Media and Corresponding Regression Coefficients ρ

λ_{irr}/nm	$\phi(\lambda_{irr}/nm)$ (ρ)	
	Water	Methanol
254	0.028 (0.981)	0.0052 (0.964)
313	0.014 (0.988)	0.0047 (0.999)

nal product of oxidation is formaldehyde formed from methanol [4]. In such a case, the mechanism of Fe(II) and CH_2O formation can be expressed by eqns (*B*—*E*) in which Fe(III) species are denoted as Fe^{3+} and excited states by asterisk (*)

$$Fe^{3+} \xrightarrow{h\nu} {}^*Fe^{3+} \qquad (B)$$

$${}^*Fe^{3+} \longrightarrow Fe^{3+} \qquad (C)$$

$${}^*Fe^{3+} + CH_3OH \longrightarrow Fe^{2+} + {}^\cdot CH_2OH + H^+ \qquad (D)$$

$${}^\cdot CH_2OH + Fe^{3+} \longrightarrow Fe^{2+} + CH_2O + H^+ \qquad (E)$$

The radical $^\cdot CH_2OH$ was identified in irradiated methanolic solution of $[Fe^{III}(gly)_2]^{3-}$ by spin-trapping EPR technique using DMPO and ND as spin traps. As evidenced by the computer simulation of the spectra, the adduct DMPO—CH_2OH was characterized by the coupling constants $a_N = 1.51$ mT and $a_H = 2.133$ mT, while for the adduct ND—CH_2OH the constants $a_N = 1.395$ mT and $2 \times a_H = 0.773$ mT were determined.

Two conclusions can be derived from eqns (*B*—*E*). The first one is that the absorption of a photon by the Fe(III) complex can lead, as a maximum, to the formation of two Fe(II) species. It might happen when nonredox deactivation of excited $^*Fe^{3+}$ (process (*C*)) does not occur and the reactions (*D*) and (*E*) are realized with 100 % efficiency. The second conclusion is that the relation $c(Fe^{2+}):c(CH_2O) \geq 2$ must be valid. The sign > relates to the systems, in which $^\cdot CH_2OH$ radicals disproportionate to CH_3OH and CH_2O or produce an adduct product (*e.g.* OH—CH_2—CH_2—OH) without interaction with and reduction of Fe(III) species. In the presence of Fe(III) this kind of the radical reactions is not common [4] and our HPLC measurements did not show any presence of dimeric or polymeric product of the radicals. The mole ratio, determined in our systems, indicates clearly that along with the above presented "standard stoichiometric" oxidation of methanol there is another source of formaldehyde in the irradiated methanolic solutions of $[Fe^{III}(gly)_2]^{3-}$ complex. The only species participating in the production of additional formaldehyde is coordinated glyphosate. The involvement of glyphosate can be realized by at least two modes. Firstly, glyphosate ligand itself can serve as a source of carbon for the formaldehyde formation. This possibility is supported by the identification of formaldehyde in irradiated aqueous solutions. Secondly, radical product(s) of the primary photoredox step(s) or subsequent thermal decomposition redox processes can oxidize molecules of methanol to formaldehyde. Noncoordinated glyphosate cannot be directly excited by a photon absorption or by energy transfer due to the absence of any suitable energy levels for such an excitation. Along with processes (*B*—*E*), other, probably nonstoichiometric processes, occur in irradiated aerated aqueous solutions of the complex, which can be described, based on identification of their products, by the scheme

$${}^*[Fe^{III}(gly)_2]^{3-} \longrightarrow xCH_2O + yNH_3 + \\ + z\text{P-containing product(s)} + \qquad (F)$$

Inhibitory effect of glyphosate complexation to the central atom Fe(III) on its function is a known phenomenon [1]. The photochemical decomposition of coordinated glyphosate is an important factor of its ecological aspects and agricultural application which has not been studied in detail so far. It should be pointed out that the photoreduction of Fe(III) to Fe(II) can be associated either with an outer sphere oxidation of a molecule present in the secondary coordination sphere (*e.g.* a molecule of methanol when methanolic solutions are irradiated) or with an inner sphere oxidation and decomposition of a glyphosate ligand. At any rate, Fe(III) must be present in an irradiated system. It was a reason for longer-lasting (up to several hours) irradiation of oxygen-containing systems of the complex $[Fe(gly)_2]^{3-}$

Decomposition of coordinated glyphosate ligand was proved *via* identifying ammonia and formaldehyde in irradiated aqueous solutions of the complex $[Fe(gly)_2]^{3-}$ The assumed decrease in the total glyphosate content in the irradiated solutions was followed by HPLC and NMR. An HPLC instrument used in our laboratory, equipped for electrochemical or optical detection of species present in investigated systems, allows to identify glyphosate. The low detector response to glyphosate compared with its high response to OH^- ions [6] does not, however, permit to follow changes in the glyphosate concentration with the irradiation time since the uncertainty in the determination exceeded the extent of the changes.

As a further, more suitable method to follow changes of glyphosate concentration with time of irradiation, ^{31}P NMR was chosen. This method allows to identify various phosphorus-containing species in cases of different bonding and environment of phosphorus atoms. The results obtained can be rationalized as follows. The total amount of glyphosate in irradiated systems gradually decreases with the time of irradiation (for data for a time dependence at certain specific conditions see Table 2). Decoupled ^{31}P NMR

Table 2. Dependence of the Integral Intensity of a ^{31}P NMR Glyphosate Peak (*vs.* the Peak Intensity of an Internal Standard) and Values of Glyphosate Concentration on Time of Irradiation for an Irradiated (λ_{irr} = 254 nm, I_o(254 nm) = 1.23 × 10^{-6} N_A $h\nu$ s^{-1}) Aqueous Solution with the Initial Concentrations $c(Fe^{III})$ = 1.60 × 10^{-3} mol dm^{-3}, $c(H_3gly)$ = 1.00 × 10^{-2} mol dm^{-3}, c(NaOH) = 2.00 × 10^{-2} mol dm^{-3} in the Presence of Oxygen

t_{irr}/min	0	5	10	35	95
Relative integral intensity	1.739	1.567	1.525	1.519	1.390
10^3 × $c(H_3gly)$/(mol dm^{-3})	10.00	9.01	8.77	8.74	7.99

spectra of irradiated basic solutions consist of peaks with the chemical shifts δ = 17.28 and 3.62, which were attributed to glyphosate and the internal standard, respectively, and two new peaks localized at δ = 20.11 and 5.99, which provide an evidence of the formation of two phosphorus-containing species during irradiation. The strong pH dependence of chemical shifts in ^{31}P NMR spectra, which is a general feature of ^{31}P NMR spectra [7], has not, however, allowed us to attribute unambiguously the new peaks to specific phosphorus-containing species. The work in this direction is in progress.

The above results lead to a formulation of some conclusions. The bleaching associated with the absorption of a photon by the complex $[Fe(gly)_2]^{3-}$, observed by the flash photolysis method, seemingly contradicts to the increase of the absorbance, found at the steady-state irradiation. However, it should be pointed out that the processes occurring in the time domain of minutes (the changes in the absorbance and its decrease during the steady-state irradiation) cannot be followed by the flash experiments applied (the time domain of nanoseconds). The bleaching may be rationalized as a consequence of the formation of short-lived Fe(II) species which is subsequently reoxidized to Fe(III). Another possibility, which should not be *a priori* excluded, is the heterolytic splitting of a bond between the central atom Fe(III) and a ligand donor atom yielding a short-lived Fe(III) complex with a lower coordination number and thus with a lower molar absorption coefficient, because the absorption in the UV region is of LMCT nature (roughly speaking, the smaller number of oxygen donor atoms, the lower probability of a charge transfer from a ligand to the central atom).

The increase of the absorbance in the UV region, observed during the first phase of continuous irradiation cannot be caused by the Fe(III) photoreduction since the only species absorbing radiation at λ > 250 nm in the irradiated systems are Fe(III) complexes. Photosubstitution of a tridentate glyphosate ligand in the excited complex with solvent molecules is very improbable due to both the necessity to split simultaneously three bonds and the short lifetime of Fe(III) complexes in their LMCT states (usually the lifetime $\tau < 10^{-9}$ s). We proposed a tentative explanation stemming from the known structural variability of glyphosate complexes [3]. The absorption of a photon by the most stable isomeric form of the complex in its ground state can lead through a partial dissociation and subsequent recoordination of a glyphosate ligand to the formation of a less stable isomer of the complex with higher absorptivity in the UV region. Such kind of photoinduced isomerizations is a well documented phenomenon in photochemistry of coordination compounds [8]. Any isomeric forms of the complex $[Fe(gly)_2]^{3-}$ can undergo photoreduction of Fe(III) to Fe(II) and the course of this reaction was followed in all the investigated systems in the absence of oxygen. It seems to be worth mentioning that Fe(III) complexes belong to the category of substitutionally labile compounds and in their isomerizations more species can be involved.

The efficiency of photochemically induced glyphosate decomposition in aqueous oxygen-containing systems (the corresponding quantum yield, based on NMR data, is ϕ_{gly} = 3.4 × 10^{-2}) is of the same order as that of Fe(II) formation in deaerated systems. A known decrease of the herbicidal activity of glyphosate with time in soil can thus be understood as a consequence of two main factors. The first one is the ability of glyphosate to coordinate to metal cations present in soil. The other factor of the activity decreasing is the photochemical degradation of coordinated glyphosate. In assessing the importance of the latter factor, the spectrum of solar radiation must be taken into account.

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