



Gamma-ray induced degradation of diazinon and atrazine in natural groundwaters

K.A. Mohamed, A.A. Basfar*, A.A. Al-Shahrani

Radiation Technology Center, Atomic Energy Research Institute, King Abdulaziz City for Science and Technology, P.O. Box 6086, Riyadh 11442, Saudi Arabia

ARTICLE INFO

Article history:

Received 30 March 2008

Received in revised form 20 October 2008

Accepted 25 November 2008

Available online 3 December 2008

Keywords:

Radiolytic degradation

Diazinon

Atrazine

Natural groundwaters

Decontamination

ABSTRACT

Degradation of diazinon and atrazine pesticides present in natural groundwaters was investigated on a laboratory scale upon γ -irradiation from a ^{60}Co source. The effects of pesticide type, initial concentration, characteristics of natural groundwater, potential radical scavengers and absorbed dose on efficiency of pesticide degradation were investigated using GC–MS. γ -Irradiation experiments were carried out for three concentrations (i.e. 0.329, 1.643 and 3.286 μM /diazinon and 0.464, 2.318 and 4.636 μM /atrazine) with irradiation doses over the range 0.5–5.6 kGy for diazinon and 0.2–21 kGy for atrazine. γ -Radiolysis showed that diazinon was much easier to degrade by ionizing radiation compared to atrazine in all natural groundwater samples. This was observed at the three initial concentrations over the range irradiation doses. The irradiation doses required for degradation of 50 and 90% diazinon (distilled water) and atrazine (humic aqueous solution) at the three concentrations were not sufficient to degrade the same concentrations in different natural groundwater samples. Moreover, the presence of naturally occurring inorganic scavengers in solutions of diazinon and atrazine decreased significantly the efficiency of radiolytic degradation of pesticides, especially at higher concentrations.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Worldwide usage of pesticides has increased dramatically during the last two decades, coinciding with changes in farming practices and increasingly intensive agriculture. This widespread use of pesticides for agricultural and non-agricultural applications resulted in the presence of their residues in various environmental matrices.

Pesticide contamination of surface and groundwaters has been well documented worldwide and constitutes an issue of great concerns on national, regional, and global levels [1–4]. Diazinon and atrazine are among the most frequently occurring phosphorothioate and triazine pollutants in natural waters. These compounds and their metabolites were encountered during monitoring studies in various aquatic systems all over the world [5–10].

For purification of polluted natural waters, numerous advanced oxidation technologies are under investigation or in use. These technologies are based on the generation of $\text{OH}\cdot$ radicals, which break down organic pollutants. The use of radiation treatment to protect and conserve the environment has been widely discussed in recent years. Ionizing radiation has been used in order to induce degradation for a wide variety of organic pollutants in aqueous solutions

[11–17]. In addition, this technology was used for the treatment of drinking water [18]. In our previous work, degradation of diazinon insecticide/nematicide and atrazine herbicide contaminated water solutions was investigated during γ -irradiation and by-products of radiolytic degradation were identified [19,20].

The aim of this study was to extend research work on distilled water solutions to natural groundwaters to investigate the influence of naturally inorganic scavengers in natural groundwaters on efficiency of radiolytic degradation of diazinon and atrazine pesticides.

2. Materials and methods

2.1. Chemicals

Two pesticides were used in the present study: diazinon (phosphorothioate group of insecticide/nematicide) and atrazine (triazine group of herbicide) were purchased from Ehrenstorfer Quality (EQ), Augsburg, Germany. Humic acid technical substance was obtained from Fluka, Germany. All solvents used were of highest available purity and were used as received (Merck, Aldrich).

2.2. Irradiation source

A Cobalt-60 γ -rays source model Gamma Cell 220 from MDS Nordion, Canada was used for all irradiation studies. The source was

* Corresponding author. Tel.: +966 1 481 3648; fax: +966 1 481 3887.
E-mail address: abasfar@kacst.edu.sa (A.A. Basfar).

Table 1

Diazinon and atrazine detection and characteristics of distilled and natural groundwater used for all experiments.

Parameter	MCL (mg L ⁻¹)	DW	Groundwater samples						
			GW1	GW2	GW3	GW4	GW5	GW6	
Diazinon	0.02 ^a	ND	ND	ND	ND	ND	ND	ND	ND
Atrazine	0.005 ^b	ND	ND	ND	ND	ND	ND	ND	ND
NH ₃	–	ND	ND	ND	ND	ND	ND	ND	ND
NO ₂	0.005	ND	ND	ND	ND	ND	ND	ND	ND
NO ₃	45 ^a	5.8	12.4	64.7 ^c	83.6	142.7 ^c	221.4 ^c	230 ^c	230 ^c
TDS	≤500 ^d	3.8	336	850 ^c	1640 ^c	2220 ^c	2360 ^c	4300 ^c	4300 ^c
Cl ⁻	≤250 ^d	1	62	132	381 ^c	632 ^c	591 ^c	1068 ^c	1068 ^c
SO ₄ ²⁻	≤500 ^d	20	124	275	1205 ^c	1622 ^c	1354 ^c	2490 ^c	2490 ^c
CaCO ₃	500	6	154	338	509 ^c	781 ^c	831 ^c	1624 ^c	1624 ^c
Ca ⁺	200	0.8	68	141	142	140	169	380 ^c	380 ^c
Mg ⁺	150	ND	12.2	47	89	92	101	103	103
Fe ²⁺	≤0.3 ^d	ND	ND	ND	ND	ND	ND	ND	ND
F	1.5 ^a	0.6	0.5	ND	0.7	ND	0.98	1.4	1.4
HCO ₃	–	1	56	71	74	79	82	172	172
E.C (mho/cm)	160–1600	9.2	55	153	324	430	454	855	855
pH	6.5–8.5 ^d	6.8	8.1	7.4	7.2	7.1	7.3	7.7	7.7

MCL: maximum contaminant level (see Ref. [27]).

–: parameters without guidelines.

ND: not detected.

DW: distilled water.

GW: groundwater.

^a Maximum acceptable concentration.^b Interim maximum acceptable concentration.^c Values higher than MCL.^d Aesthetic objective.

calibrated using aqueous ferrous sulfate (Fricke dosimetry) solution [11]. Dose rate was 14.52 kGy h⁻¹ and transit dose was estimated to be 5.86 Gy. All of the irradiations were conducted at room temperature, 23 °C. In addition, all of the diazinon and atrazine aqueous solutions were irradiated over the range 0.2–21 kGy.

2.3. Experimental procedures

Investigation of radiolytic degradation of diazinon and atrazine pesticides in six natural groundwater samples collected from different locations in Riyadh Province in Saudi Arabia was conducted. The six groundwater samples were subjected to an evaluation to detect residues of diazinon and atrazine as well as characteristics of samples (Table 1).

A half liter sample from each type of tested groundwater was placed in a volumetric flask and fortified with diazinon to reach the three initial concentrations of (0.329, 1.643 and 3.286 μM). Humic substances (HS) aqueous solutions (200 mg L⁻¹) were prepared in the six groundwater samples. Solutions were filtered, and then sodium bicarbonate (1 g L⁻¹) was added in the aqueous solutions of HS. Atrazine was introduced in prepared solutions to reach atrazine initial concentrations of (0.464, 2.318 and 4.636 μM). Diazinon and atrazine solutions were placed in 40 mL vials having airtight caps with teflon based silicon septa. The prepared solutions were irradiated in these vials at two absorbed doses $D_{0.5}$ and $D_{0.9}$ (dose required to remove 50 or 90% of initial diazinon and/or atrazine concentration). These doses were established previously for diazinon in distilled water [19] and atrazine in HS aqueous solutions [20] using γ -irradiation (Table 2). Immediately after irradiation, extraction was employed using dichloromethane according to the official methods adopted by Letizia et al. [21]. Gas chromatography combined with mass spectrometer (GC–MS) was used for pesticides analysis. The recovery of this procedure was not less than 90%.

2.4. Gas chromatography/mass spectrometer (GC/MS) analysis

A Shimadzu 2010 series GC with QP2010 mass spectrometer and HP-5 capillary column (Hewlett Packard, 30 m, 0.25 mm I.D.,

0.25 μm film thickness) was used for gas chromatography analysis. The carrier gas (helium) velocity was 40 cm/s, high pressure injection was set at ON and high pressure and injection pressure was set at 250 kPa. The temperatures of injector, ion source and interface were set at 250, 200 and 250 °C, respectively and the oven program was 2 min at 80 °C, 20 °C min⁻¹ to 180 °C (2 min) and 5 °C min⁻¹ to 250 °C (5 min). Ions were formed for mass spectrometric detection using ion electron impact ionization (EI⁺) mode scan. EI⁺ mass spectra database searches were carried out using the Wiley Registry of Mass Spectral Data, and the NIST Mass Spectral Search Program. The concentrated extract (4 μL aliquots) was injected splitless under pesticides detection limit of 0.003 μM (diazinon) and 0.005 μM (atrazine).

All measurements were performed in triplicates, and the tabulated results represent mean values. Based on the analytical data, the corresponding degradation percents were calculated and discussed.

3. Results and discussion

An important consideration in extending experiments in distilled water solutions to natural groundwater samples, for all AOPs,

Table 2Summary of $D_{0.5}$ and $D_{0.9}$ values for the diazinon (DW) and atrazine (HS) used in the groundwater experiments.

Pesticide	Concentration (μM)	Dose (kGy)		Reference
		$D_{0.5}$	$D_{0.9}$	
Diazinon	0.329	0.5	1.5	[19]
	1.643	1.5	5	
	3.286	1.7	5.6	
Atrazine	0.464	0.2	0.6	[20]
	2.318	1	4	
	4.636	6	21	

$D_{0.5}$: represents the dose (kGy) required for degradation of 50% diazinon (DW) and/or atrazine (HS).

$D_{0.9}$: represents the dose (kGy) required for degradation of 90% diazinon (DW) and/or atrazine (HS).

Table 3
Rate constants ($M^{-1} s^{-1}$) of chemical species commonly found in natural waters with transient reactive species formed during irradiation of aqueous solutions.

Chemical species	Rate constants		
	e_{aq}^-	H^*	OH^*
Bicarbonate ion	1.0×10^6	4.0×10^4	8.5×10^6
Carbonate ion	3.5×10^5	NR	3.9×10^8
Chloride	NR	NR	4.2×10^9
Sulfate	1.0×10^6	NR	
Bromide ion	NR	2.8×10^7	1.1×10^{10}
Nitrate ion	9.7×10^9	1.4×10^6	NF
Nitrite ion	3.5×10^9	7.1×10^8	1.0×10^{10}
Oxygen	1.9×10^{10}	2.1×10^{10}	NR

NR: not reported.

is the influence of radical scavengers (i.e. carbonate, bicarbonate, nitrate and nitrite ions) on removal of the pollutants of interest. In addition, natural constituents of natural groundwaters must be considered so they may not compete with the contaminants for the reactive species (i.e. e_{aq}^- , H^* and OH^*). Table 3 presents ions which can reduce treatment efficiency by acting as radical scavengers [22–24].

It is well known that the presence of these species of scavengers in natural groundwaters may affect the degradation of diazinon and atrazine aqueous solutions during irradiation at two absorbed doses ($D_{0.5}$ and $D_{0.9}$). These doses were established previously for diazinon in distilled water using γ -irradiation showing 0.5, 1.5 and 1.7 kGy ($D_{0.5}$) and 1.5, 5 and 5.6 kGy ($D_{0.9}$) at three diazinon concentrations (0.329, 1.643 and 3.286 μM), respectively [19]. In addition, atrazine in HS aqueous solutions showing 0.2, 1 and 6 kGy ($D_{0.5}$) and 0.6, 4 and 21 kGy ($D_{0.9}$) at three atrazine concentrations (0.464, 2.318 and 4.636 μM), respectively was irradiated [20].

Results indicate the influential role of pesticide type, initial concentration, characteristics of natural groundwaters, potential radical scavengers and absorbed dose on the radiolytic degradation of diazinon and atrazine. Results of each pesticide will be discussed separately in the next sections.

3.1. Radiolytic degradation of diazinon

From the results in Figs. 1 and 2, the influence of groundwater characteristics on radiolytic degradation of phosphorothioate diazinon at the three concentrations was observed. Radiolytic degradation of diazinon varied among the natural groundwater samples. This was observed in the three concentrations (0.329, 1.643 and 3.286 μM) at absorbed doses over the range 0.5–1.7 kGy (representing $D_{0.5}$ values) and over the range 1.6–5.6 kGy (representing $D_{0.9}$ values). Degradation percentages at $D_{0.5}$ were 49.2, 47.1, 44.1, 40.1, 41 and 38% (0.329 μM /0.5 kGy); 48.4, 45.2, 45.4, 40.6, 37.8 and 34.4% (1.643 μM /1.5 kGy) and 45.1, 41.9, 40.4, 34.5, 35.8 and 32.2% (3.286 μM /1.7 kGy) corresponding to six groundwa-

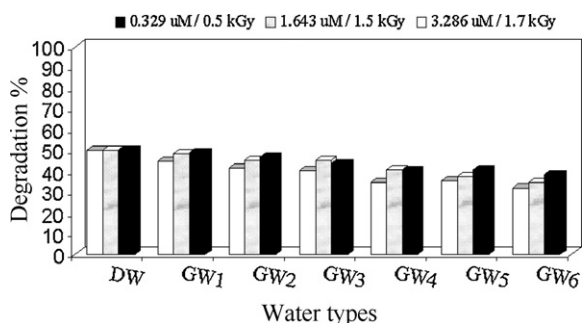


Fig. 1. Degradation efficiencies of diazinon at three concentrations in different types of natural groundwaters at $D_{0.5}$.

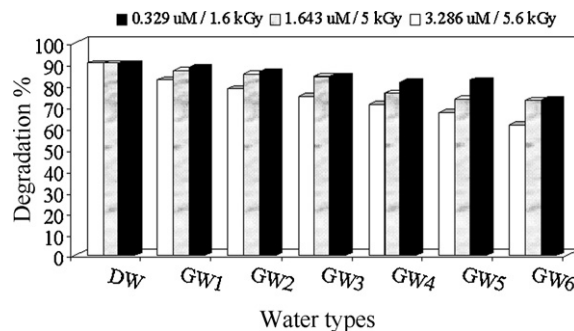


Fig. 2. Degradation efficiencies of diazinon at three concentrations in different types of natural groundwaters at $D_{0.9}$.

ter samples GW1, GW2, GW3, GW4, GW5 and GW6, respectively. The degradation percentages at $D_{0.9}$ reached 88.1, 86, 83.9, 81.2, 82.1 and 72.9% (0.329 μM /1.6 kGy); 86.4, 85, 83.8, 76.2, 73.6 and 72.6% (1.643 μM /5 kGy) and 82.2, 78, 74.4, 70.7, 66.9 and 61.5% (3.286 μM /5.6 kGy) for the six groundwater samples, respectively.

Taking the degradation percentage of diazinon (0.329 μM /1.6 kGy) in distilled water as a base line (1.0) for comparison, the relative degradation ratio of diazinon are 0.979, 0.956, 0.932, 0.902, 0.912 and 0.81 corresponding to the six groundwater samples, respectively. Moreover, when taking the degradation percentage of diazinon (3.286 μM /5.6 kGy) in distilled water as a base line (1.0) for comparison, the relative radiolytic degradation ratios of diazinon are 0.913, 0.867, 0.827, 0.786, 0.743 and 0.683 for the six groundwater samples, respectively. These ratios reflect the influence of the initial concentration and the characteristics of natural groundwater on the radiolytic degradation of diazinon.

Because of the presence of many potential radical scavengers in natural groundwaters, it can be concluded that such scavengers like carbonate, bicarbonate and nitrite ions inhibit the radiolytic degradation of diazinon and this trend is more pronounced at high concentrations of these scavengers. According to rate constants in Table 2, $K(OH^* + CO_3^{2-}) = 3.9 \times 10^8 M^{-1} s^{-1}$, $K(OH^* + HCO_3^-) = 8.5 \times 10^6 M^{-1} s^{-1}$ and $K(OH^* + NO_2^-) = 1.1 \times 10^{10} M^{-1} s^{-1}$ [22–24], it is obvious that the reaction of OH^* radicals with CO_3^{2-} , HCO_3^- and NO_2^- and consequently radiolytic degradation of diazinon decreases with the increase of scavengers concentrations due to competition reactions of diazinon and scavengers for OH^* radicals. However, rate constants of these scavengers with diazinon are not available in the literature.

Considering the maximum residues limits (MRLs) of diazinon in drinking water (0.066 μM) [25], it is realized that the initial concentration of diazinon of (0.329 μM) represents five folds of MRL value. An irradiation dose of 1.6 kGy was enough to decrease the diazinon concentration to levels lower than diazinon MRLs in drinking water. This trend was observed in all natural groundwater samples except (GW6) which reached 0.089 μM after irradiation. In addition, a different trend was observed at high concentrations of diazinon of 1.643 μM (25 folds MRL) and 3.286 μM (50 folds MRL) where irradiation doses up to 5 and 5.6 kGy were not enough to decrease diazinon concentrations to levels less than MRLs for all natural groundwater samples.

3.2. Radiolytic degradation of atrazine

Effect of absorbed doses from 0.2 to 6 kGy ($D_{0.5}$ values) and from 0.6 to 21 kGy ($D_{0.9}$ values) on the radiolytic degradation of herbicide atrazine prepared in HS aqueous solutions at an initial concentrations of 0.464, 2.318 and 4.636 μM was investigated in

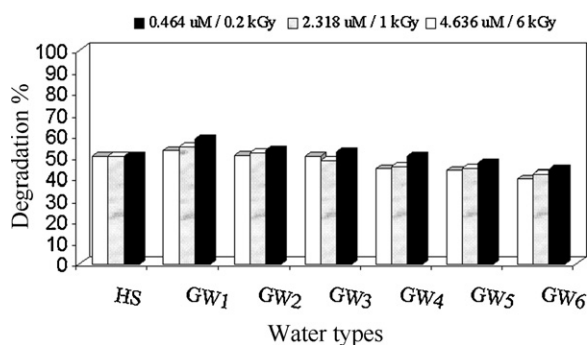


Fig. 3. Degradation efficiencies of atrazine at three concentrations in different types of natural groundwaters at $D_{0.5}$.

different natural groundwater samples and the results are shown in Figs. 3 and 4. As a result of irradiation, a significant change of atrazine concentrations was observed, although degradation behavior of atrazine herbicide varied among the natural groundwater samples. It can be seen that the radiolytic degradation of atrazine is slightly higher for two groundwater samples (i.e. GW1 and GW2) compared to other samples. This finding was observed in the three concentrations with absorbed doses over the range 0.2–6 kGy.

Degradation percentages at $D_{0.5}$ were 58, 53, 51.9, 50, 47 and 44% (0.464 $\mu\text{M}/0.2$ kGy); 54.8, 51.6, 48, 45.4, 44.2 and 41.6% (2.318 $\mu\text{M}/1$ kGy) and 52.8, 50.3, 50.2, 44.1, 43.6 and 39.5% (4.636 $\mu\text{M}/6$ kGy) corresponding to the six groundwater samples (i.e. GW1, GW2, GW3, GW4, GW5 and GW6), respectively. On the other hand, degradation percentages at $D_{0.9}$ were 92, 87.9, 84.9, 78, 73.1 and 65.9% (0.464 $\mu\text{M}/0.6$ kGy); 89.8, 86.9, 81.8, 73.2, 68.8 and 64.6% (2.318 $\mu\text{M}/4$ kGy) and 86, 85.8, 74.4, 68.1, 67.6 and 60% (4.636 $\mu\text{M}/21$ kGy) corresponding to the six groundwater samples, respectively.

By considering the degradation percentage of atrazine (0.464 $\mu\text{M}/0.6$ kGy) in humic substance aqueous solution (HS) as a base line for comparison (1.0), the relative radiolytic degradation ratios are 1.022, 0.977, 0.943, 0.867, 0.812 and 0.732 for the six groundwater samples, respectively. In addition, atrazine concentration plays also an important role in the radiolytic degradation of atrazine. When taking the degradation percent of atrazine (4.636 $\mu\text{M}/21$ kGy) in (HS) as a base line for comparison (1.0), the relative degradation ratios are 0.956, 0.953, 0.827, 0.757, 0.751 and 0.667 for the six groundwater samples, respectively. These ratios demonstrate the important role of the initial concentration and the characteristics of natural groundwater samples in the decontamination of atrazine in water.

The presence of carbonate (>509 mg L^{-1}), bicarbonate (>74 mg L^{-1}) and nitrate anions (>84 mg L^{-1}) with atrazine hindered significantly the efficiency of the degradation of atrazine

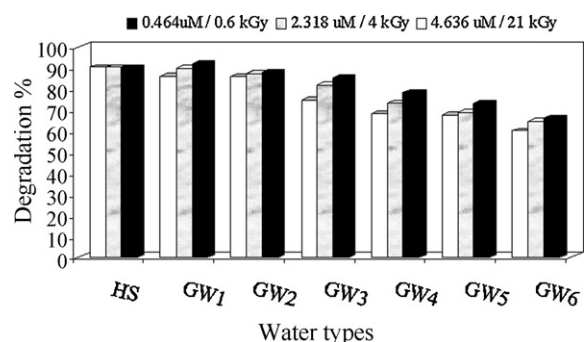


Fig. 4. Degradation efficiencies of atrazine at three concentrations in different types of natural groundwaters at $D_{0.9}$.

especially at higher concentrations (2.318 and 4.636 μM with 1 and 6 kGy, respectively). On the other hand, the presence of these ions under the previous levels resulted in the enhancement of radiolytic degradation of atrazine ($\geq 8\%$) at the lower atrazine concentration (0.464 $\mu\text{M}/0.2$ kGy).

However, as total alkalinity is increased, concentration of carbonate and bicarbonate ions increased, and the OH^\bullet radicals decreased via reaction with carbonate (3.9×10^8 $\text{M}^{-1} \text{s}^{-1}$) and bicarbonate (8.5×10^6 $\text{M}^{-1} \text{s}^{-1}$) ions [22]. Another common scavenger of OH^\bullet radicals in groundwater is nitrite which react with OH^\bullet and convert to nitrate (1×10^6 $\text{M}^{-1} \text{s}^{-1}$) ions [13,22]. On the other hand, the rate constants for solvated electrons (e_{aq}^-) with carbonate, bicarbonate and nitrate ions were determined as 3.5×10^5 $\text{M}^{-1} \text{s}^{-1}$, 1.0×10^6 $\text{M}^{-1} \text{s}^{-1}$ and 9.7×10^9 $\text{M}^{-1} \text{s}^{-1}$, respectively [22–24], consequently a decrease of solvated electrons was expected. In addition, the rate constant for reaction of OH^\bullet with atrazine was determined as 3.0×10^9 $\text{M}^{-1} \text{s}^{-1}$ [26], whereas the rate constant for reaction of solvated electrons (e_{aq}^-) with atrazine was determined as 4.8×10^9 $\text{M}^{-1} \text{s}^{-1}$ [17]. Moreover the radiolytic behavior of atrazine in water is not totally clear whether it follows oxidation reactions [13] or reduction reactions [17,20] and consequently radiolytic degradation of atrazine decreases with increase of groundwater scavengers concentrations due to competition reactions of atrazine and scavengers for OH^\bullet radicals and solvated electrons (e_{aq}^-).

Results demonstrated the influence of a variety of groundwater components (mainly carbonate, bicarbonate, nitrite and nitrate ions) in the reduction of atrazine degradation, the higher the scavenger ions concentrations in groundwater the lower the radiolytic degradation and vice versa. Therefore, the concentrations of these scavengers should be taken into account during radiolytic degradation of organic pollutants in contaminated waters and they should also be decreased before irradiation.

Considering the interim maximum acceptable concentrations (IMACs) of atrazine herbicide and its metabolites in drinking water, it can be concluded that the concentration of atrazine/HS aqueous solutions like, (0.464 μM) represents 20 folds IMACs value. An irradiation dose of 0.6 kGy was not sufficient to decrease the atrazine initial concentration to levels lower than atrazine IMACs in drinking water which is established at 0.023 μM [25]. This trend was observed with all natural groundwater samples. In addition, the same trend was observed at high concentrations of atrazine of 2.318 μM (100 folds IMACs) and 4.636 μM (200 folds IMACs) even after irradiation doses up to 4 and 21 kGy. Such high doses were not sufficient to decrease concentrations to levels less than IMACs for all natural groundwater samples.

4. Conclusions

The removal of diazinon and atrazine pesticides from natural groundwaters using ^{60}Co gamma-irradiation is influenced by groundwaters characteristics. Diazinon was much easier to degrade by radiation compared to atrazine in all groundwater samples. Degradation of diazinon varied among the groundwater samples and this was observed for the three concentrations at absorbed doses from 0.5 to 5.6 kGy. The presence of the radical scavengers in natural groundwater like carbonate, bicarbonate, and nitrite ions inhibits the radiolytic degradation of diazinon and this effect become more pronounced at high concentrations of these scavengers and pesticide. An irradiation dose of 1.6 kGy was sufficient to decrease the diazinon concentration (0.329 μM) to levels lower than diazinon MRLs in drinking water (0.066 μM); this trend was observed in the all groundwater samples except one. On the other hand, degradation behavior of atrazine varied among the natural groundwater samples. The radiolytic degradation of atrazine

was slightly higher for two groundwater samples (GW1 and GW2) compared to other samples. This finding was observed in the three concentrations with absorbed doses over the range 0.2–6 kGy. The presence of carbonate ($>509 \text{ mg L}^{-1}$), bicarbonate ($>74 \text{ mg L}^{-1}$) and nitrate ($>84 \text{ mg L}^{-1}$) in the irradiated groundwater samples (GW4–GW6) hindered significantly the efficiency of the radiolytic degradation of 2.318 and 4.636 μM atrazine with absorbed doses of 1 and 6 kGy, respectively. Furthermore, an irradiation dose of 0.6 kGy was not sufficient to decrease the lower initial concentration of atrazine to levels lower than atrazine IMACs in drinking water which is established at 0.023 μM and their finding was observed in all groundwater samples studied. Moreover, the irradiation doses required for degradation of 50 and 90% diazinon (distilled water) and atrazine (humic aqueous solution) at the three initial concentrations were not sufficient to degrade the same concentrations in all groundwater samples. This has to be always considered in practical application of this technology for radiolytic removal of pesticides from waters. For potable water, gamma-irradiation may be used directly to degrade the organic contaminants, but in case of groundwaters, the concentrations of these scavengers should be decreased by conventional methods before irradiation.

Acknowledgement

Authors extend their appreciation to King Abdulaziz City for Science and Technology (KACST) for funding this project.

References

- [1] A. Huber, M. Bach, H.G. Frede, Pollution of surface waters with pesticides in Germany: modeling non-point source inputs, *Agric. Ecosyst. Environ.* 80 (2000) 191–204.
- [2] M.J. Cerejeira, P. Viana, S. Batista, T. Pereira, E. Silva, M.J. Valerio, A. Silva, M. Ferreira, A.M. Silva-Fernandes, Pesticides in Portuguese surface and ground waters, *Water Res.* 37 (2003) 1055–1063.
- [3] A. Székács, A. Ernst, J. Juracek, B. Darvas, Monitoring water polluting pesticides in Hungary, in: E. Elbestawy, L. Moklyachuk, V. Pidlisnyuk, N. Schulz, T. Stefanovska, J. Vijgen (Eds.), 7th International HCH and Pesticides Forum Book, International HCH & Pesticides Association, Holte, Denmark, 2005, pp. 68–69.
- [4] E. Maloschik, A. Ernst, G. Hegedüs, B. Darvas, A. Székács, Monitoring water-polluting pesticides in Hungary, *Microchem. J.* 85 (2007) 88–97.
- [5] J.L. Domagalski, N.M. Dubrovsky, Pesticide residues in ground water of the San Joaquin Valley, California, *J. Hydrol.* 130 (1992) 299–338.
- [6] H.G.K. Ordelman, Watersystemverkenningen. Een analyse van de problematiek in aquatisch milieu. RIZA nota 93.036, 1993.
- [7] T.A. Albanis, D.G. Hela, T.M. Sakellarides, I.K. Konstantinou, Monitoring of pesticide residues and their metabolites in surface and underground waters of Imathia (N. Greece) by means of solid-phase extraction disks and gas chromatography, *J. Chromatogr. A* 823 (1998) 59–71.
- [8] H. Baily, L. Deanovic, E. Reyes, T. Kimball, K. Larson, K. Cortright, V. Conner, D. Hinton, Diazinon and chlorpyrifos in urban waterways in Northern California, USA, *Environ. Toxicol. Chem.* 19 (2000) 82–87.
- [9] S. Garcia, C. Ake, B. Clement, H. Huebner, K. Donnelly, S. Shalat, Initial results of environmental monitoring in the Texas Rio Grande valley, *Environ. Int.* 26 (2001) 465–474.
- [10] T. Wolfgang, J. Groeneweg, B. Jantsch, Diffuse atrazine pollution in German aquifers, *Biodegradation* 13 (2002) 3–10.
- [11] R.J. Woods, A.K. Pikaev, *Applied Radiation Chemistry*, John Wiley and Sons, New York, 1994.
- [12] A.K. Pikaev, I.E. Makarov, A.V. Ponomarev, Y. Kim, B. Han, Y.W. Yang, H.J. Kang, A combined electron-beam and coagulation method of purification of eater from dyes, *Mandeliev Commun.* 5 (1997) 176–178.
- [13] N. Karpel Vel Leitner, B. Pascale, G. Peter, Gamma-irradiation for the removal of atrazine in aqueous solution containing humic substances, *Radiat. Phys. Chem.* 55 (1999) 317–322.
- [14] G. Angelini, R. Bucci, F. Carnevaletti, M. Colosimo, Radiolytic decomposition of aqueous atrazine, *Radiat. Phys. Chem.* 59 (2000) 303–307.
- [15] A.A. Basfar, H.M. Khan, A.A. Al-Shahrani, Trihalomethane treatment using gamma irradiation: kinetic modeling of single solute and mixture, *Radiat. Phys. Chem.* 72 (2005) 555–563.
- [16] A.A. Basfar, H.M. Khan, A.A. Al-Shahrani, W.J. Cooper, Radiation induced decomposition of methyl *tert*-butyl ether in water in presence of chloroform: kinetic modeling, *Radiat. Phys. Chem.* 39 (2005) 2085–2095.
- [17] R. Varghese, H. Mohan, P. Manoj, V.M. Manoj, U.K. Aravind, K. Vandana, C.T. Aravindakumar, Reaction of hydrated electrons with triazine derivatives in aqueous medium, *J. Agric. Food Chem.* 54 (2006) 8171–8176.
- [18] N. Getoff, Advancements of radiation induced degradation of pollutants in drinking and waste water, *Appl. Radiat. Isot.* 40 (1989) 585–594.
- [19] A.A. Basfar, K.A. Mohamed, A.J. Al-Abduly, T.S. Al-Kurajji, A.A. Al-Shahrani, Degradation of diazinon contaminated waters by ionizing radiation, *Radiat. Phys. Chem.* 76 (2007) 1474–1479.
- [20] A.A. Basfar, K.A. Mohamed, A.J. Al-Abduly, A.A. Al-Shahrani, Radiolytic degradation of atrazine aqueous solution containing humic substances, *Ecotoxicol. Environ. Saf.*, in press, doi:10.1016/j.ecoenv.2008.05.006.
- [21] M.D. Letizia, B. Massimo, P. Luciano, L. Michelina, Evaluation of the membrane approach to solid-phase extraction of pesticides residues in drinking water, *Pestic. Sci.* 35 (1992) 63–67.
- [22] P. Neta, R.E. Huie, A.B. Ross, Rate constants for reactions of inorganic radicals in aqueous solutions, *J. Phys. Chem.* 17 (1988) 1027–1111.
- [23] W.J. Cooper, R.A. Dougal, M.G. Nickelsen, T.D. Wait, C.N. Kurucz, K. Lin, J.P. Bibler, Benzene destruction in aqueous waste part 1. Bench-scale gamma irradiation experiments, *Radiat. Phys. Chem.* 48 (1996) 81–87.
- [24] R.A. Dougal, W.J. Cooper, M.G. Nickelsen, K. Lin, T.D. Waite, C.N. Kurucz, J.P. Bibler, Industrial-scale destruction of benzene in a simulated mixed waste using electron-beam irradiation, in: W.J. Cooper, R.D. Curry, O'Shea (Eds.), *Environmental Applications of Ionizing Radiation*, John Wiley & Sons, Inc., New York, 1998, pp. 417–427.
- [25] D.J. Hamilton, A. Ambrus, R.M. Dieterle, A.S. Felsot, C. Harris, P. Holland, A. Katayama, N. Kurihara, J. Linder, J. Unsworth, S. Wong, Regulatory limits for pesticides residues in water. IUPAC technical report, *Pure Appl. Chem.* 75 (2003) 1123–1155.
- [26] A. Tauber, C. von Sonntag, Products and kinetics of the OH-radical-induced dealkylation of atrazine, *Acta Hydrochim. Hydrobiol.* 28 (2000) 15–23.
- [27] Summary of Guidelines for Canadian Drinking Water Quality, Prepared by the Federal–Provincial Subcommittee on Drinking Water of the Federal–Provincial–erritorial Committee on Environmental and Occupational Health, March 2001.