

Photocatalytic degradation of metoxuron in aqueous suspensions of TiO₂. Analytical and kinetic studies

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ABSTRACT. The photocatalytic degradation of metoxuron [3-(3-chloro-4-methoxyphenyl)-1,1-dimethylurea] in aqueous suspensions of TiO₂ was investigated. Several intermediate photoproducts were identified using NMR and MS techniques. Oxidation or removal of the methyl of terminal nitrogen and ring hydroxylation were found to occur. 2-Propanol was shown to decrease the rate of photocatalytic degradation, inhibiting partly ring hydroxylation and completely reactions on terminal nitrogen. In contrast, basification of the suspensions accelerated the degradation significantly. Degussa P25 TiO₂ was found to exhibit a higher photocatalytic activity than Millennium TiO₂ in spite of a generally smaller specific surface area. Within the Millennium TiO₂ series, the photocatalytic efficiency increased with the specific surface area.

1. INTRODUCTION

Metoxuron (MX) is a selective herbicide absorbed by the leaves and roots and acting as photosynthetic electron transport inhibitor at the photosystem II receptor site [1]. The toxicity is moderate : the acute oral LD50 is around 3200 mg/kg in rats. The biodegradation is a relatively slow process, DT₅₀ in soils being around 10–30 days. Transformation upon light exposure was also shown to be slow [2]. The main reaction was found to be photohydrolysis of the C – Cl bond with formation of 3-(3-hydroxy-4-methoxyphenyl)-1,1-dimethylurea. It was also shown that the toxicity of metoxuron solutions on marine bacterium *Vibrio fischeri* increased in the course of the irradiation time.

Photocatalytic degradation mediated by illuminated semiconductor particles suspended in aqueous solutions has been proven to be an efficient elimination pathway of organic pollutants [3]. Titanium dioxide and zinc oxide have been studied mostly as photocatalysts. Electron-hole pairs are formed under photoexcitation of the photoactive oxide in the near UV. Oxygen is reduced into O₂^{•-} by electrons promoted in the conduction band and positive holes oxidize OH⁻ or H₂O into hydroxyl radicals that are very powerful oxidants. Substrates can be oxidized either by hydroxyl radicals or by positive holes.

In the present work, the photocatalytic degradation of metoxuron over aqueous suspensions of TiO₂ was investigated. In a first step, product studies were performed in order to identify the intermediate photoproducts. Then, the photocatalytic degradation

of metoxuron was studied at various pH values and in the presence of 2-propanol. In a last step, we compared Degussa P25 TiO₂ and Millennium TiO₂ exhibiting various specific surface areas for their ability to photocatalyse the degradation of metoxuron.

2. MATERIALS AND METHODS

2.1. Reactants. Metoxuron (99.6% purity) was purchased from Riedel-de-Haën and used as received. 2-Propanol was of the highest grade available. Degussa P25 TiO₂ was 70 : 30 (anatase : rutile) with a specific surface area of 55 m² g⁻¹. TiO₂-Tiona PC 50, PC 100, PC 105 and PC 500 were all provided by Millennium Inorganic Chemicals. They showed specific surface areas (BET method) equal to 45 ± 5 m² g⁻¹, 85 ± 10 m² g⁻¹, 90 ± 10 m² g⁻¹ and > 250 m² g⁻¹, respectively. Millennium titanium dioxides were mainly anatase. Water was purified using a Milli-Q device (Millipore).

2.2. Irradiations. Irradiations of aqueous suspensions of TiO₂ were performed in a cylindrical Pyrex glass reactor (20 mm i.d × 240 mm high) using a fluorescent lamp (Philips TLAD 15 W/05) emitting within the wavelength range 300–450 nm with a maximum of emission at 365 nm. The device had an cylindrical shape with elliptical base and was equipped with reflecting walls. The reactor and the lamp were located on both focal axes. Suspensions consisted of 15 ml of aqueous metoxuron (5 × 10⁻⁴ M–10⁻⁴ M) and typically 1 g L⁻¹ of TiO₂. Experiments were carried out under aerobic conditions and the temperature of reactor was maintained at 15 ± 3 °C by water circulation. Suspensions were stirred 20 minutes prior to irradiation and during

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the irradiation. Aliquots of suspensions (around 400 μl) were sampled at the end of the adsorption period (20 min) and during irradiation at selected intervals. The particles were removed by filtration on cellulose acetate filters (Sartorius) prior to HPLC analyses. pH of suspensions were 4.8 ± 0.1 when TiO_2 was added at a level of 1 g L^{-1} . Acidification and basification were achieved by adding HClO_4 and borate buffers respectively.

2.3. Analyses. Losses of MX and formation of photoproducts were monitored by HPLC using a Waters chromatograph (model 990) equipped with a photodiode array detector and a conventional C18 reverse phase column ($5 \mu\text{m}$, $100 \text{ mm} \times 24 \text{ mm}$). The eluent was a mixture $\text{MeOH}/\text{H}_2\text{O}$ (50 : 50, v/v). Samples were injected three times. Semi-preparative HPLC was performed on a Gilson apparatus equipped with a C18 Microsorb column ($3 \mu\text{m}$, $250 \text{ mm} \times 4.6 \text{ mm}$). Collected fractions were evaporated to dryness. Half of each fraction was dissolved in methanol and analysed by desorption chemical ionization mass spectrometry and the other part was dissolved in CDCl_3 and analysed by NMR. The intermediate photoproducts exhibited similar UV spectra with maxima around 240 and 290 nm. Their concentrations in irradiated samples were evaluated assuming that they had molar absorption coefficient at 240 nm similar to metoxuron. This calculation method allows an informative but rough estimation of photoproduct concentrations.

$^1\text{H-NMR}$ spectra were recorded on a Bruker 400 MHz. Experiments in desorption chemical ionization mass spectrometry were conducted on a HP 5989 B mass spectrometer. Methane was used as ionization gas.

3. RESULTS AND DISCUSSION

3.1. Photocatalytic degradation of metoxuron over Degussa P25 TiO_2 . As shown in Figure 1A, aqueous MX (10^{-4} M) was photolysed very slowly when irradiated alone at $\lambda > 300 \text{ nm}$. Addition of TiO_2 (1 g L^{-1}) significantly increased the rate of MX disappearance. The amount of MX adsorbed over the photocatalyst in the dark was evaluated as to be 2–3%. It can be concluded that the loss of MX was almost exclusively due to photochemical processes.

The typical HPLC chromatogram of an irradiated sample is given Figure 2. Six main intermediate photoproducts were found after a conversion extent of 35%. These photoproducts were separated by semi-preparative HPLC and identified on the basis of $^1\text{H-NMR}$ and $\text{CH}_4 - \text{CI}$ -mass spectrometry data (see Table 1). Proposed structures are given in Figure 3. MS data of the most polar fraction revealed the presence of a chlorinated compound through the presence of M and M + 2 in the ratio 1 : 3 and also of a dechlorinated compound. The former, that shows the mass of metoxuron less 28, is likely to be

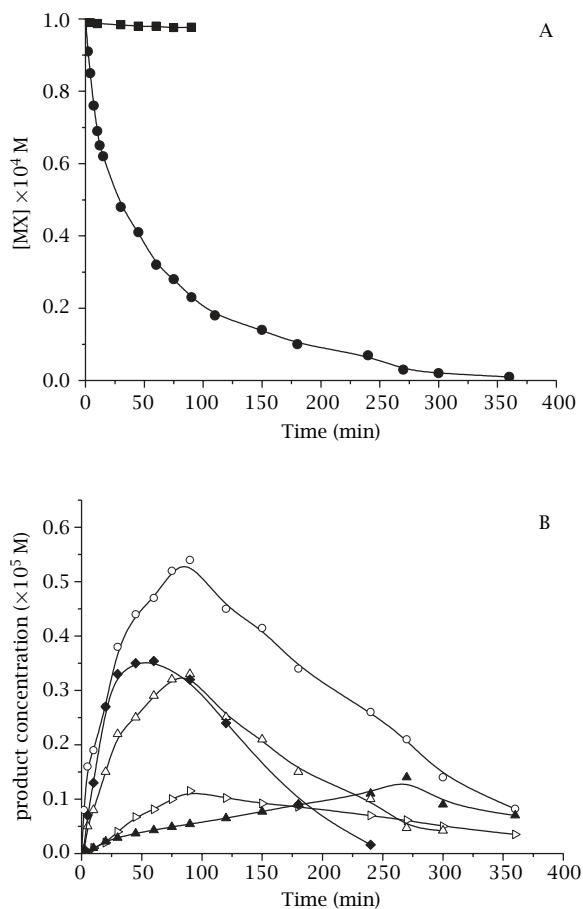


Figure 1. (A) Phototransformation of metoxuron (10^{-4} M) when irradiated in pure water (■) or in the presence of Degussa P25 TiO_2 (1 g L^{-1}) (●). (B) Evolution of photoproducts vs the irradiation time; 1 + 2 (▷); 3 (○); 4 (▲); 5 (△); 6 (◆).

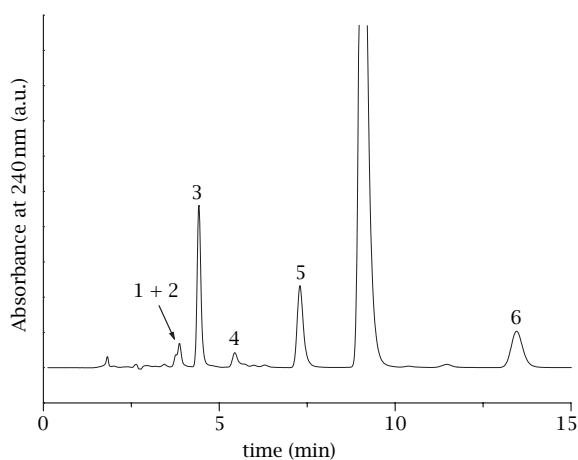


Figure 2. HPLC chromatogram of a solution of metoxuron ($5 \times 10^{-4} \text{ M}$) irradiated in the presence of Degussa P25 TiO_2 (1 g L^{-1}). Conversion extent = 35%.

Table 1. CH₄ – CI mass spectrometry and ¹H-NMR data of metoxuron and photoproducts. TiO₂ Degussa P25.

Products	Molecular ions m/z (main fragments)	¹ H-NMR data (δ ppm) in CDCl ₃
metoxuron	229/231 [M + H] ⁺ (184/186), 257/259 [M + 29] ⁺ and 269/271 [M + 41] ⁺	
1	201/203 [M + H] ⁺ and 229/231 [M + 29] ⁺	
2	211 [M + H] ⁺ (166) and 239 [M + 29] ⁺	
3	215/217 [M + H] ⁺ (170/172), 243/245 [M + 29] ⁺ and 255/257 [M + 41] ⁺	7.55 (d, 1H, J = 2, 5 Hz); 7.06 (dd, 1H, J = 8.9 and 2.5 Hz); 6.93 (d, 1H, J = 8.8 Hz); 3.05 (s, 6H)
4	229/231 [M + H] ⁺ , 257/259 [M + 29] ⁺ and 269/271 [M + 41] ⁺	10.6 (s, 1H); 7.7 (d, 1H, J = 2.5 Hz); 7.24 (dd, 1H, J = 8.9 and 2.5 Hz); 6.98 (d, 1H, J = 8.9 Hz); 3.3 (s, 3H).
5	215/217 [M + H] ⁺ (184/186), 243/245 [M + 29] ⁺ and 255/257 [M + 41] ⁺	7.34 (d, 1H, J = 2.6 Hz); 7.17 (dd, 1H, J = 8.8 and 2.5 Hz); 6.95 (d, 1H, J = 8.8 Hz); 3.5 (s, 3H); 2.7 (s, 3H).
6	243/245 [M + H] ⁺ (215/217 and 184/186), 271/273 [M + 29] ⁺ and 283/285 [M + 41] ⁺	10.6 (s, 1H); 7.65 (d, 1H, J = 2.6 Hz); 7.38 (dd, 1H, J = 8.8 and 2.5 Hz); 6.90 (d, 1H, J = 8.8 Hz); 3.3 (s, 3H); 2.95 (s, 3H).

the N-di-demethylated compound (photoproduct 1) while the latter that is fragmented into the 3-(3-hydroxy-4-methoxyphenyl)-isocyanate (165) should be the 3-(3-hydroxy-4-methoxyphenyl)-1,1-dimethylurea (photoproduct 2). Compounds 3 and 5 showed same m/z values. However, they could be differentiated on the basis of their fragmentation. Photoproduct 3 gave a fragment at m/z = 170 and 172 consistent with 3-(3-chloro-4-hydroxyphenyl)-isocyanate while 5 a fragment at m/z = 184 and 186, consistent with 3-(3-chloro-4-methoxyphenyl)-isocyanate as in the case of metoxuron. Moreover, NMR data showed the presence of the two equivalent methyl groups in 3 (singlet corresponding to six protons) while two signals corresponding each at three protons were obtained for 5. It shows that the missing methyl group is that of methoxy in product 3 and that of urea in 5. Photoproduct 6 could be identified unambiguously : the m/z value and the NMR data proves the oxidation of a methyl into CHO [4]. NMR data of photoproduct 4 proved the removal of a first methyl group and the oxidation of a second into CHO; in agreement the m/z values at 229 and 231 correspond to the mass of metoxuron after elimination of CH₂ and 2H and addition of O. The analogy of chemical shifts of aromatic protons between 4 and 6 shows that only methyls of terminal nitrogen were affected.

This analytical study indicates that the photocatalytic degradation of metoxuron proceeds via oxidation or removal of the methyl groups linked to the terminal N (photoproducts 1, 4, 5, 6) and substitution of Cl or OMe by OH (photoproducts 2 and 3).

Figure 1B gives the evolution of photoproducts concentration vs the irradiation time. It clearly appears that photoproducts 1–6 were photodegraded in turn. The complete mineralisation of metoxuron is therefore expected to occur. 3 was produced in the highest yield.

The concentration reached a maximum (5.5×10^{-6} M) after 90 min of irradiation, i.e. when MX conversion was 85%. 6 and 5 were formed in slightly lower amounts (maximum equal to 3.5×10^{-6} M and 3.2×10^{-6} M respectively). The concentrations were maximum after 50 and 90 min of irradiation respectively. 1 + 2 and 4 were produced in much lower amounts and 4 reached a maximum concentration after more than 250 min in line with a secondary formation.

3.2. Influence of 2-propanol. As shown in Figure 4, 2-propanol was found to inhibit the photocatalytic transformation of MX when added within the range 0.4–1.2%. This result was expected since hydroxyl radicals are known to contribute to the oxidation of metoxuron and 2-propanol to trap them efficiently [5, 6]. The addition of 2-propanol affected the formation of photoproducts in different ways (Table 2). Ring hydroxylation (photoproducts 2 and 3) was only partly inhibited while oxidation or removal of methyl groups of terminal nitrogen was completely inhibited (photoproducts 4, 5 and 6). These results are reminiscent to those obtained previously when we studied the influence of 2-propanol on the photocatalytic oxidation

Table 2. Product distribution in the absence and in the presence of 2-propanol. [MX] = 10⁻⁴ M; Degussa P25 TiO₂ (1 g L⁻¹); pH = 4.6; conversion extent 34%.

Percentage of 2-propanol (%)	Irradiation time (min)	Chemical yield of photoproducts (%)*				
		1 + 2	3	4	5	6
0	10	6.1	8.5	0.9	0.33	3.8
0.4	20	1.7	2.8	-	-	-
0.8	30	1.2	2.5	-	-	-
1.2	40	1.1	0.6	-	-	-

* uncertainties are about 10%.

Table 3. Dependence of the chemical yields of photoproducts (%) on pH. $[MX] = 10^{-4} M$; Degussa P25 $TiO_2 (1 g L^{-1})$.

	Irradiation time (min)	Conversion extent (%)	Chemical yields of photoproducts (%) [*]					
			1 + 2	3	4	5	6	X
pH = 2.0	20	38	0.6	12	0.9	1.3	5.3	Significant amount
pH = 4.8	10	31	0.9	13	1.19	4.5	4.2	-
pH = 9.5	5	31	0.9	15	traces	4.8	3.2	-

* uncertainties are about 10%.

of phenolic compounds in aqueous ZnO suspension : the hydroxylation in *ortho* position was shown to be completely inhibited by 2-propanol while hydroxylation in *para* position was only partly inhibited [7, 8].

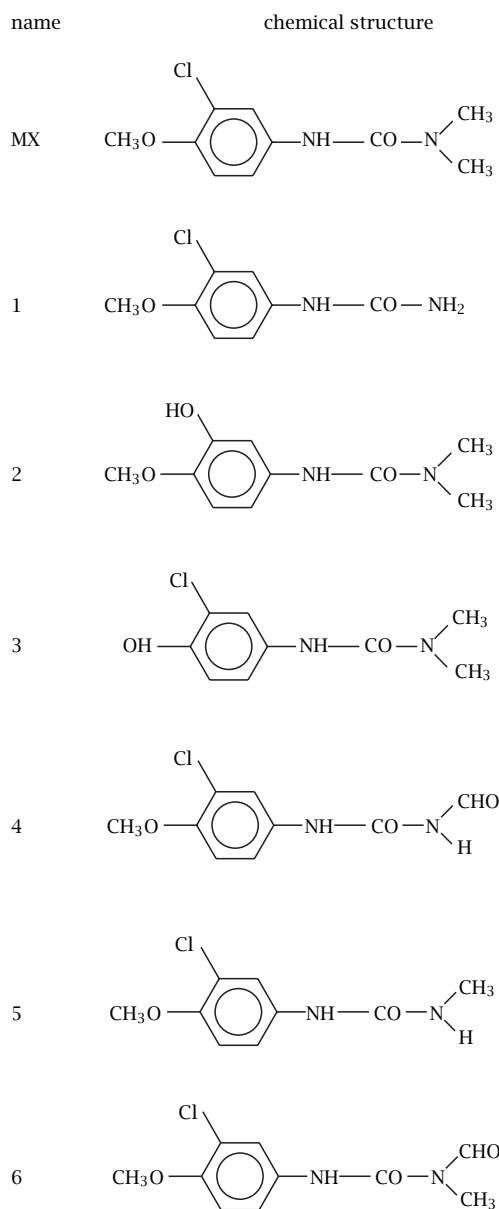


Figure 3. Structure of metoxuron and photoproducts.

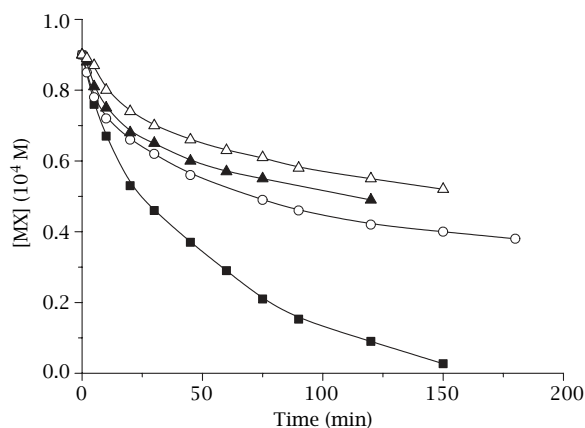


Figure 4. Phototransformation of metoxuron ($10^{-4} M$) when irradiated on Degussa P25 $TiO_2 (1 g L^{-1})$ in the absence of propanol (■) and in the presence of 2-propanol : 0.4% (○); 0.8% (▲); 1.2% (△).

This observation was interpreted in terms of selectivity in positive holes and hydroxyl radicals attacks. In the same way, we could deduce that hydroxyl radicals oxidize both the ring and the methyl groups of metoxuron while positive holes only the ring. Such a selectivity might be due to the way MX is adsorbed on the surface. In the hypothesis that MX is adsorbed by the ring moiety, the methyl groups are kept away from the surface and their oxidation by positive holes is therefore unfavoured. In contrast, hydroxyl radicals that are mobile species could oxidize all oxidable sites whatever the position of the molecule on the surface.

3.3. Influence of pH. The photocatalytic degradation of MX was studied at several pH values : at natural pH (4.8), in acidic medium (pH = 2) and in basic medium (pH = 9.5), from both kinetic and analytical point of views. The rate of phototransformation was found to increase as the pH was increased (see Figure 5). This enhancing effect that was previously reported in the literature can be attributed in part to a more efficient formation of hydroxyl radical from OH^- than from water [9].

Changing the pH had only a small effect on the product distribution (see Table 3). A decrease of pH from 9.5 to 2.0 slightly favoured the formation of 6

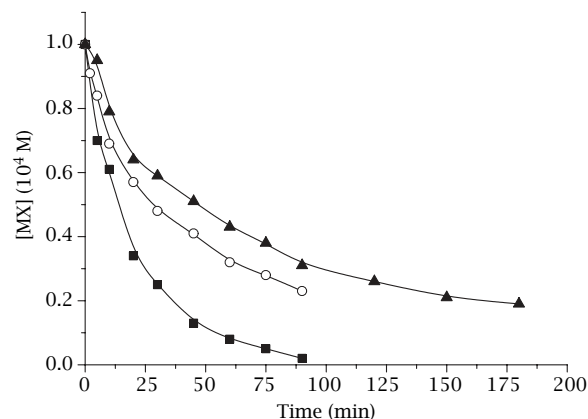


Figure 5. Phototransformation of metoxuron (10^{-4} M) when irradiated on Degussa P25 TiO_2 (1 g L^{-1}) at pH = 2 (\blacktriangle), at pH = 4.8 (\circ) and at pH = 9.5 (\blacksquare).

but unfavoured that of 3. The formation of 5 was more significantly reduced upon acidification from 4.8 to 2.0. Clearly a new photoproduct was observed at pH = 2.

3.4. Compared photocatalytic efficiency of various TiO_2 . The photocatalytic efficiency of the Degussa P25 TiO_2 was compared to that of Millennium TiO_2 (see Figure 6). Degussa P25 TiO_2 was found to

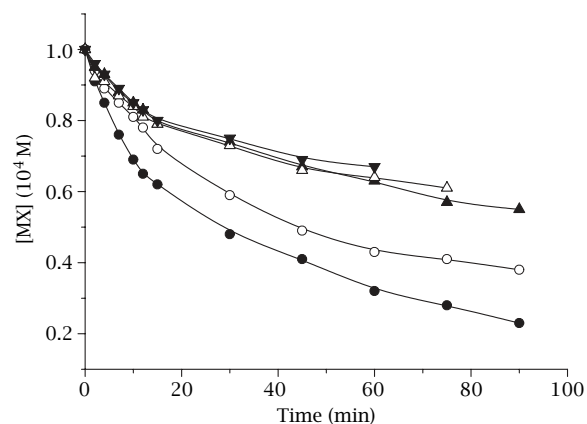


Figure 6. Phototransformation of metoxuron (10^{-4} M) in the presence of various TiO_2 (1 g L^{-1}): Degussa P25 (\bullet); Tiona PC 50 (\blacktriangledown); Tiona PC 100 (\triangle); Tiona PC 105 (\blacktriangle); Tiona PC 500 (\circ).

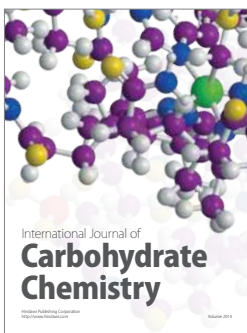
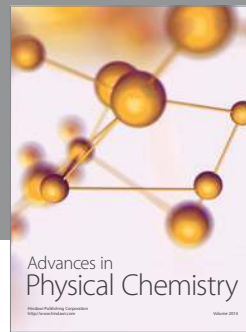
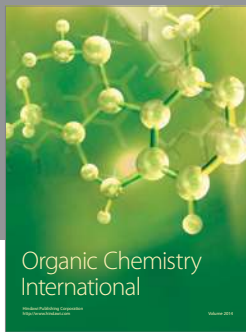
be the most efficient despite the fact that it shows a specific surface area generally smaller than the other photocatalysts. Tiona PC 50, PC 100 and PC 105 had similar photocatalytic activity while their specific surface area vary within the range $45\text{--}90 \text{ m}^2 \text{ g}^{-1}$. Only an enhancement of the photocatalytic activity was found with Tiona PC 500 that exhibits a very large specific surface area. These results indicate that the specific surface area is not the only factor influencing the activity of photocatalysts. The density of superficial defects favouring the recombination of electrons with positive holes might be another factor influencing this activity.

4. CONCLUSION

We show that the degradation of metoxuron in aqueous medium can be achieved using TiO_2 as photocatalyst. The primary photoproducts are photodegraded in turn and complete mineralisation should occur. The reaction is accelerated upon basification while inhibited by 2-propanol. Degussa P25 TiO_2 is more efficient than Millennium TiO_2 despite the fact that its specific surface area is lower. Studies are in progress to confirm and understand these differences.

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