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Stability of malathion, diazinon and chlorpyrifos in different water types – a review

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Stabilnost malationa, diazinona i klorpirifosa u različitim vrstama voda – pregledni rad

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ABSTRACT

Prior to their application, most pesticide formulations should be mixed with water to form a spray of the required concentration. The efficiency of the active substance in the spray solutions could be affected by the quality of the used water, whose composition is related to its source (e.g., rain, river, stream, lake, tap and ground water) and sampling season (spring-autumn). Temperature and pH, as well as other water quality parameters, could significantly affect the pesticide stability in spray by promoting the pesticide degradation rate. This review aims to summarize and discuss degradation data of three widely used organophosphorus insecticides (malathion, diazinon and chlorpyrifos) in different types of water in order to emphasize the influence of different water types on their degradation. This review also reveals a lack of studies that can confirm the effect of other water quality parameters, except temperature and pH, on the stability of pesticides susceptible to hydrolysis.

Keywords: organophosphorus pesticides; pesticide degradation; half-life; hydrolysis; water quality

SAŽETAK

Većinu formulacija pesticida je potrebno pomiješati s vodom prije njihove primjene radi pripreme škropiva potrebne koncentracije. Na učinkovitost aktivne tvari u škropivu može utjecati kvaliteta vode, jer sastav vode može varirati ovisno o izvoru vode (npr. kišnica, rijeka, potok, jezero, voda iz slavine i podzemna voda) i vremenu uzorkovanja (proljeće-jesen). Temperatura i pH vrijednost te drugi parametri kvalitete vode mogu utjecati na stabilnost pesticida u škropivu poticanjem razgradnje u vodi. Pregledni rad ima za cilj sažeti i raspraviti podatke o razgradnji triju često korištenih organofosfornih insekticida (malationa, diazinona i klorpirifosa) u različitim vrstama voda, te naglasiti utjecaj različitih vrsta voda na njihovu razgradnju. Ovaj pregledni rad također otkriva nedostatak studija koje bi mogle potvrditi učinak drugih parametara kvalitete vode, osim temperature i pH, na stabilnost pesticida koji podliježu hidrolizi.

Ključne riječi: organofosforni pesticidi, razgradnja pesticida; vrijeme poluraspada; hidroliza, kvaliteta vode

INTRODUCTION

According to Regulation (EC) No 1107/2009, pesticides are plant protection products (PPPs) used for protecting plants or plant products against all harmful organisms or preventing the action of such organisms, among other uses defined.

Commercial PPPs are formulated as mixtures of at least one active substance and substances added as adjuvants, safeners, synergists or co-formulants. Many of these formulations are liquid concentrates or wettable powders, which should be mixed with water to form an aqueous spray emulsion, suspension or solution of a required concentration according to the label.

As water may account for as much as 95% of the spray, the water quality can significantly affect the stability of the active substance used in the spray (Whitford et al., 2009). Considering that the time between spray preparation and spray application can be longer than several hours, the amount of active substance in spray can be reduced and result in a poor effect on harmful organisms. Natural water of different origin can have significantly different amounts of dissolved mineral ions, organic matter and pH reaction (Schilder, 2008).

In a neutral to moderately acidic environment, most active substances are stable, while their hydrolysis rate can be promoted in alkaline conditions. The degradation rate primarily depends on the chemical properties of the active substance (its susceptibility), temperature and alkalinity of the water and contact time of pesticide with water in the sprayer tank (Deer and Beard, 2001; Cloyd, 2015).

The kinetic studies of the active substance degradation rate in aqueous solutions are carried out under controlled laboratory conditions and the active substance persistence has usually been expressed by their half-lives (DT_{50}) corresponding to the time in which 50% of the active substance molecules will be decomposed, i.e. the effectiveness of the pesticide that will be halved (Cloyd, 2015).

Insecticides are considered more susceptible to hydrolysis than other pesticides, particularly the chemical class of organophosphates (Deer and Beard, 2001; Schilder, 2008).

Water quality

Water quality includes the physical, chemical and biological properties of water (Liu et al., 2009). Considering water as the carrier of a pesticide, water quality has to be optimal for a certain pesticide to achieve the highest performance of that pesticide.

The alkalinity of natural waters highly depends on the availability of carbon dioxide, carbonates and hydrogen carbonates (Vugrin, 2019). Deer and Beard (2001) showed that most surface and ground water sources across the United States have a pH between 7 and 9, while Frank et al. (1991) reported that surface and ground waters in southern Ontario were in the pH range of 8-8.5. Kralj (2017) reported a pH that ranged 6.66-8.27 for ground waters in Croatia (2010-2013). According to data of the State Water Monitoring in the Republic of Croatia (2017-2020), pH levels of river waters ranged 6.8-8.8, and were alkaline in most cases (Croatian Waters, 2020).

Alkalinity can be used as an indicator of carbonate, bicarbonate and hydroxide concentrations (Kralj, 2017). Alkalinity in natural waters could originate from carbonates, hydrogen carbonates, hydroxides, silicates, borates, phosphates and hydrogen sulfides by the dissolution of mineral substances in the soil and atmosphere (Vugrin, 2019).

Hardness of water reflects the content of calcium and magnesium ions, but when they form other compounds with chlorides and nitrates, this also contributes to the overall hardness (Kralj, 2017). Most ground water samples taken in this study conducted in eastern Croatia could be characterized as hard waters (Kralj, 2017).

Salinity is the amount of salt dissolved in a body of water. The salinity correlates positively with both the alkalinity and hydrogen carbonate concentration in water, while the concentration of calcium is mostly related to total hardness of water (Kralj, 2017). Electrical conductivity (EC) is a measurement of water's ability to conduct electricity indicating the total concentration of dissolved substances in water. Total dissolved substances are the sum of mobile ions, including mineral substances, salts or metals dissolved in water. High EC is usually caused by runoff containing fertilisers salt that reached the water source (McDougall, 2012). Because dissolved ions increase salinity as well as conductivity, the two measures are related.

The content of some elements such as nitrates, calcium, chloride and suspended solids can be significantly affected by season (Alberto et al., 2001). A study into the surface water of the dam reservoirs in Turkey showed that water quality parameters more often demonstrate temporal differences (dry and wet season) than spatial differences, with higher values of the temperature and pH in dry season and higher values of the total hardness, electrical conductivity and alkalinity in the wet season (Varol et al., 2011).

Effect of water quality on pesticides

Water quality can negatively affect pesticide solubility and absorption by the target pest, but farmers may not be aware of the significance of water quality (Whitford et al., 2009). An inadequate water pH (pH>7) can lead to the decomposition of the active substance and poor effectiveness of the product by reducing the required dose available to the pest thereafter. Low pesticide rates may favour mutation rates leading to pesticide resistance (Gressel, 2011) and stimulating the growth and other conditions favourable to harmful organisms, a phenomenon known as hormesis (Duke et al., 2017).

Pesticides are often subjected to hydrolysis under alkaline conditions, a chemical breakdown of substances in water with a loss of their pesticide properties (Cloyd, 2015). At the same time, increased water temperature generally supports pesticide degradation, but this effect also depends on the water type.

In hard water, some pesticide molecules can react with ions such as iron, aluminium, calcium, magnesium, and sodium, and form new molecules or complexes that are not able to penetrate into harmful organisms and suppress their action (Whitford et al., 2009). Generally, hardness has a negative effect on insecticide stability in water or persistence of activity on harmful organisms (Oxley et al, 1997).

High levels of salinity (electrical conductivity above 500 µS/cm) may also result in the deactivation of certain chemicals (Gordon and Betts, 2014).

Some dissolved metal ions in water such as copper, zinc, cobalt, magnesium, and mercury may catalyse degradation of pesticides, especially of organophosphorus insecticides (Liu et al., 2001).

The free oxygen contained in surface waters may increase the pesticide biodegradation rate (Aydinalp and Porca, 2004).

Turbid water with a “muddy” appearance and high content of suspended solids, soil, or organic matter, can also reduce the effectiveness of some pesticides (Griffin, 2009).

ORGANOPHOSPHORUS INSECTICIDES

The use of organophosphorus insecticides started in 1947 (Tjosvold and Karlik, 2003) with parathion and malathion being the first organophosphate pesticides to be synthesized in the United States (Adeyinka et al., 2002). Organophosphorus pesticides are still widely used in many countries (Figure 1).

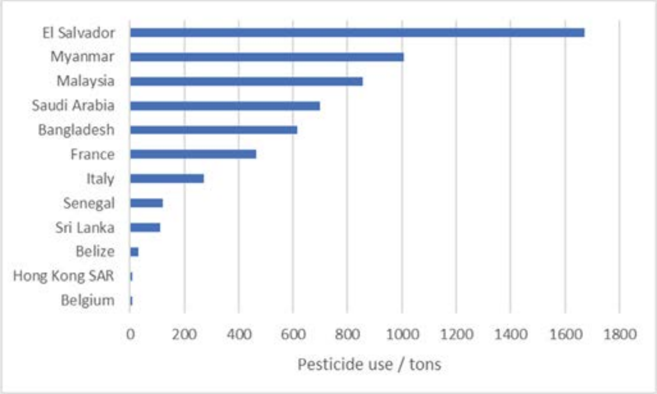

Figure 1. Use of organophosphorus insecticides in 2020 (FAO, 2023)

Organophosphorus pesticides are used to control insects in crops with a common mechanism of action by inhibiting acetylcholinesterase (AChE) enzymes (Neylon et al., 2022). They are mostly not persistent in the environment but are toxic to non-target organisms such as aquatic organisms (Zainuddin, 2020).

Malathion was approved for use in the European union (EU) in 2010 as an insecticide in greenhouses, currently with authorisation in Greece and Italy (EC, 2022). The active substance is also authorised in the United States and used in agriculture all over the world (Tchounwou, 2015). Among organophosphorus insecticides, diazinon and malathion are the most frequently used ones in agriculture and its residues can be detected in the environment, especially in water resources (Khaghani and Zare, 2019).

Diazinon is widely used in agricultural and non-agricultural activities, including Iran (Behrooz et al., 2021), Costa Rica, (SFE, 2022), Brazil (Anvisa, 2023), Chile (APD, 2022), China (Meiling, 2022), Russia (AGROXXI.RU, 2023) and Malaysia (Pesticide Control Division, 2023). Diazinon is banned in the EU (EC, 2022), Argentina, and India (AgroPages, 2023). In the United States, diazinon was one of the most widely used insecticides available on the residential market before 2000, but after 2002 all indoor residential uses of diazinon products were prohibited. Diazinon is now authorized only for use on selected fruits, vegetables and nuts, and for ornamentals grown outdoors in nurseries (EPA, 2008).

Chlorpyrifos has been heavily used worldwide since 1965 (Hu, 2018). In 2008, chlorpyrifos products were authorised for use in more than 88 countries (ECHA, 2022). Chlorpyrifos is still in wide use in Brazil (Anvisa, 2023), Chile (Ministry of Health, 2023), Costa Rica (SFE, 2022), Hong Kong (AFCD, 2020), Indonesia (Agriculture Quarantine Agency, 2023), Japan (JFCRF, 2023), Malaysia (Pesticide Control Division, 2023), New Zealand (Ministry for Primary Industries, 2023), Russia (AGROXXI.RU, 2023), South Africa (South African Government, 2023), Taiwan (Taiwan FDA, 2023), Uganda (MAAIF, 2023), Kenya (AgroPages, 2023), China (use on vegetables is prohibited) (CIRS, 2022), and many African countries.

Chlorpyrifos was banned in the EU in 2019 (EC, 2022), while in the United States, it was restricted in 2022, but is still used on food and animal feed crops intended for export, as long as certain conditions are met (EPA, 2022a). There are currently 31 active registrants of chlorpyrifos with 135 active product labels in the United States (EPA, 2022b). Canada revoked the remaining chlorpyrifos authorizations in 2021 (Health Canada, 2023). Australia suspended the domestic and home garden uses of chlorpyrifos products in 2019, but active substances can still be used in agriculture according to a defined label (APVMA, 2023).

The organophosphorus pesticides approved in the EU are pirimiphos–methyl, malathion and fosthiazate (EC, 2022). Many organophosphorus pesticides were withdrawn from the Croatian market following their ban at EU level, but some are still authorised in Croatia, such as pesticides containing pirimiphos–methyl and fosthiazate (Ministry of Agriculture, 2022).

Within the class of organophosphorus pesticides, the most sold organophosphorus pesticide in the period 2013–2022 (by the date it was allowed to sell) was chlorpyrifos with its total volume sold in Croatia amounting to 211,683.39 kg (Ministry of Agriculture, 2022b).

Degradation of organophosphorus pesticides in water

The degradation of organophosphorus pesticides in water can occur via oxidation, photodegradation and hydrolysis (Pehkonen and Zhang, 2002).

Organophosphorus pesticides may degrade into degradation products that retain a certain level of pest control and may exhibit higher, lesser, or similar activity to the parent pesticide (Druzina, 2007). Felsot and Pedersen (1991) reported on chlorpyrifos hydrolysis to 3,5,6-trichloro-2-pyridinol, a compound that has completely lost its insecticidal activity but is still bioactive against several fungal pathogens.

Organophosphorus pesticides are sensitive to pH and temperature, so when those factors increase, so does the degradation (Lartiges and Garrigues, 1995). The degradation rate may also vary seasonally, especially if the pH was different between seasons. The dissolved ions of some metals such as mercury, copper, cadmium and silver can promote the hydrolysis of organophosphorus pesticides (Wyer, 2008).

If there is a similar pH of different water sources, some organophosporus pesticides may persist longer in seawater (Bondarenko et all., 2004). Noblet (1997) reported a slower degradation in natural waters compared to degradation in Milli–Q water, which can be explained by partitioning into dissolved organic matter.

Malathion

Malathion is susceptible to alkaline hydrolysis in waterand is strongly dependent on temperature and pH (Wolfe et al., 1977).

The results of several studies on the degradation of malathion in different types of water are summarized in Table 1.

Malathion degraded in seawater very rapidly and proportionally to the pH increase. As the pH increased from 6.7 to 8.16, the half-lives of malathion rapidly decreased from 17.4 to 1.65 days (Wang and Hoffman,1991).

Druzina and Stegu (2007) showed that alkalinity of ground water enhanced the degradation of malathion with half-lives from 51.3 to 7.1 days.

In distilled buffered water, malathion persistence was significantly longer at pH 6.1 than at pH 7.4 (120 and 11 days, respectively) (Freed et al., 1979).

The study by Starner et al. (1999) found that variations in pH and composition of water measured between April and August had a negligible effect on the stability of malathion at 10 °C. At higher temperatures in the experiment, the pH and other water quality parameters became important stability factors resulting in a halved half-life of malathion in samples from April.

The study by Druzina and Stegu (2007) also showed the temperature effect on malathion stability in river water: malathion was faster degraded at high temperature (25 °C, DT_{50} = 19.8) than at low temperature (4 °C, DT_{50} = 77.9).

The half-life of malathion in river water was significantly longer at low temperature (6 °C, pH 7.3, DT_{50} = 55) than at high temperature (22 °C, pH 7.3, DT_{50} = 19) (Lartiges and Garrigues, 1995). The same effect was observed with filtered river water and ultrapure water. The comparison between the persistence of malathion in filtered and unfiltered river water of the same origin, temperature and pH showed a longer persistence in unfiltered river water. River water contained 9.2 mg of particulates/L able to slow down the degradation of malathion by its adsorption.

The influence of water type on malathion degradation was also studied by Druzina and Stegu (2007). Although usually faster degraded in alkaline conditions, their study showed faster malathion degradation in ground water at neutral pH (pH 7, DT_{50} = 68.6) than in alkaline river water (pH 8, DT_{50} = 77.9) at the same temperature (4 °C). River water was turbid and contained higher amounts of total organic carbon, iron, manganese, nitrates and nitrites, than ground water. As nitrates (Druzina and Stegu, 2007) and manganese dioxide (Farooq et al, 2005) can accelerate the hydrolysis of organophosphorus pesticides, it is possible that the particulates in turbid river water can slow down the breakdown of malathion.

In a study by Bondarenko et al. (2004), the slowest degradation of malathion was noticed in seawater, while the fastest was found in canyon water. The order of malathion half-lives was: canyon water < creek water < marsh water < bay water (seawater). The authors suggested that degradation of malathion was mostly abiotic and pH dependent. As the pH of the tested water sources ranged 7.98 – 8.86, it could be assumed that water quality significantly affected the degradation rates in different types of water.

Table 1. Half-lives of malathion in different water types

Water type	Temperature (°C)	pH	Half-life (days)	Reference
Groundwater	4	7	68.6	Druzina and Stegu, 2007
Groundwater	25	6	51.3	Druzina and Stegu, 2007
Groundwater	25	7	13.1	Druzina and Stegu, 2007
Groundwater	25	8.5	7.1	Druzina and Stegu, 2007
River water	4	8	77.9	Druzina and Stegu, 2007
River water	25	8	19.8	Druzina and Stegu, 2007
River water	10	7.9–8.1 (April)	16	Starner et al., 1999
River water	10	7.3–7.7 (August)	16	Starner et al., 1999
River water	25	7.9–8.1 (April)	2	Starner et al., 1999
River water	25	7.3–7.7. (August)	5	Starner et al., 1999
Filtered River water	6	7.3	53	Lartiges and Garrigues, 1995
River water	6	7.3	55	Lartiges and Garrigues, 1995
Filtered River water	22	7.3	7	Lartiges and Garrigues, 1995
River water	22	7.3	19	Lartiges and Garrigues, 1995
River water	–	8.2	0.92 (22 hours)	Wolfe et al., 1977
Creek water	21	8.02	1.6	Bondarenko et al., 2004
Creek water, sterilized	21	8.02	2.1	Bondarenko et al., 2004
Creek water	10	8.02	5.3	Bondarenko et al., 2004
Canyon water	21	8.86	0.3	Bondarenko et al., 2004
Canyon water sterilized	21	8.86	0.4	Bondarenko et al., 2004
Canyon water	10	8.86	1.0	Bondarenko et al., 2004
Marsh water	21	8.07	1.9	Bondarenko et al., 2004
Marsh water sterilized	21	8.07	2.6	Bondarenko et al., 2004
Marsh water	10	8.07	6.1	Bondarenko et al., 2004
Bay water	21	7.98	2.2	Bondarenko et al., 2004
Bay water sterilized	21	7.98	0.6	Bondarenko et al., 2004
Bay water	10	7.98	7.6	Bondarenko et al., 2004
Seawater	6	8.1	41	Lartiges and Garrigues, 1995
Seawater	22	8.1	6	Lartiges and Garrigues, 1995
Unsterile filtered seawater, (salinity 34 ppt)	20	8	2.6	Cotham and Bidleman, 1989
Sterile filtered seawater, (salinity 34 ppt)	20	8	5.3	Cotham and Bidleman, 1989

Continued. Table 1.

Water type	Temperature (°C)	pH	Half-life (days)	Reference
River estuary water, 24 ppt salinity	28	6	17.4	Wang and Hoffman, 1991
River estuary water, 24 ppt salinity	28	7	8.7	Wang and Hoffman, 1991
River estuary water, 24 ppt salinity	28	8.16	1.6	Wang and Hoffman, 1991
Distilled buffered water	37.5	7.4	1.3	Freed et al., 1979
Distilled buffered water	20	7.4	11	Freed et al., 1979
Distilled buffered water	20	6.1	120	Freed et al., 1979
Ultrapure water	6	6.1	212	Lartiges and Garrigues, 1995
Ultrapure water	22	6.1	42	Lartiges and Garrigues, 1995

It is worth noting that the marsh water and seawater showed significantly lower biochemical oxygen demand and total organic carbon content than canyon water and creek water, and canyon water had the lowest electrical conductivity.

Comparing sterile and non-sterile water samples, the persistence of malathion was longer in sterile creek water, sterile marsh water, and sterile canyon water than in respective freshwater samples, but shorter in the sterile seawater compared to non-sterile seawater (Bondarenko et al., 2004). In respect to the different water quality, a part of this effect can be associated to malathion biodegradation in non-sterile water samples.

Biodegradation effect was evident from a study by Cotham and Bidleman (1989) with non-sterile and sterile filtered seawater. At 20 °C and pH 8, the half-life of malathion in sterile seawater (DT_{50} = 5.3) was twice as long as in non-sterile seawater (DT_{50} = 2.6).

In contrast to the study where degradation in seawater was slower than in freshwater (Bondarenko et al., 2004), the conclusion of Wang and Hoffman (1991) was that hydrolysis of malathion can be increased with salinity. They concluded that the malathion degradation rate is increased in estuary waters compared to river waters.

A study by Lartiges and Garrigues (1995) with seawater also confirmed that degradation of malathion was accelerated by salinity and alkalinity. The half-life of malathion was shorter in seawater (22 °C, pH 8.1, DT_{50} = 6) than in river water (22 °C, pH 7.3, DT_{50} = 19) and filtered river water (22 °C, pH 7.3, DT_{50} = 7) at the same temperature. The longest half-life of malathion was in ultrapure water (6 °C, pH 6.1, DT_{50} = 212) which indicated that, apart from the pH and temperature, other water parameters such as hardness, suspended organic particles, dissolved ions and microorganisms may also promote the breakdown of malathion.

Diazinon

Diazinon is more stable in water than other organophosphorus pesticides (Frank et al, 1991). Diazinon persistence can be increased in seawater and it is temperature-dependent in freshwater (Bondarenko et all., 2004).

Results of several studies on the degradation of diazinon in different types of water are summarized in Table 2.

The degradation rate of diazinon in ground water was faster at pHs from 6-7 (DT_{50} = 59.2, DT_{50} = 73.7 days) than at pHs from 7-8.5 (DT_{50} = 73.7, DT_{50} = 75.3 days) at the same temperature (25 °C) (Druzina and Stegu, 2007), showing that diazinon can be more stable at a higher pH compared to other organophosphorus pesticides.

Temperature is an important factor for the degradation of diazinon as increased temperature promoted degradation in all water types: in tap water (Frank et

Table 2. Half-lives of diazinon in different water types

Water type	Temperature (°C)	pH	Half-life (days)	Reference
Groundwater	4	7	130.8	Druzina and Stegu, 2007
Groundwater	25	6	59.2	Druzina and Stegu, 2007
Groundwater	25	7	73.7	Druzina and Stegu, 2007
Groundwater	25	8.5	75.3	Druzina and Stegu, 2007
River water	4	8	182.4	Druzina and Stegu, 2007
River water	25	8	64.8	Druzina and Stegu, 2007
River water	10	7.3–7.7. (August)	134	Starner et al., 1999
River water	10	7.9–8.1 (April)	9	Starner et al., 1999
River water	25	7.3–7.7. (August)	103	Starner et al., 1999
River water	25	7.9–8.1 (April)	16	Starner et al., 1999
River water	6	7.3	181	Lartiges and Garrigues, 1995
River water	22	7.3	80	Lartiges and Garrigues, 1995
Filtered River water	6	7.3	132	Lartiges and Garrigues, 1995
Filtered River water	22	7.3	52	Lartiges and Garrigues, 1995
River water	(–4)–37	8.2–8.5	88 (light)-99 (dark)	Frank et al, 1991
Creek water	21	8.02	6.3	Bondarenko et al., 2004
Creek water, sterilized	21	8.02	51.1	Bondarenko et al., 2004
Creek water	10	8.02	25.6	Bondarenko et al., 2004
Canyon water	21	8.86	14.0	Bondarenko et al., 2004
Canyon water sterilized	21	8.86	54.9	Bondarenko et al., 2004
Canyon water	10	8.86	25.0	Bondarenko et al., 2004
Marsh water	21	8.07	6.4	Bondarenko et al., 2004
Marsh water sterilized	21	8.07	54.4	Bondarenko et al., 2004
Marsh water	10	8.07	28.3	Bondarenko et al., 2004
Bay water	21	7.98	41.0	Bondarenko et al., 2004
Bay water	10	7.98	124.0	Bondarenko et al., 2004
Bay water sterilized	21	7.98	54.5	Bondarenko et al., 2004
Seawater	6	8.1	125	Lartiges and Garrigues, 1995
Seawater	22	8.1	50	Lartiges and Garrigues, 1995
Tap water	21	8.0–8.2	14	Frank et al., 1991
Tap water	4	8.0–8.2	45	Frank et al., 1991
Ultrapure water	22	6.1	6.9	Lartiges and Garrigues, 1995
Ultrapure water	6	6.1	144	Lartiges and Garrigues, 1995

al, 1991), seawater and ultrapure water (Lartiges and Garrigues, 1995), river water and filtered river water (Lartiges and Garrigues, 1995) and groundwater and river water (Druzina and Stegu, 2007). At low temperature, diazinon was very persistent even in alkaline conditions. Diazinon was the most persistent in river water at low temperatures (Lartiges and Garrigues, 1995; Druzina and Stegu, 2007). In tap water, diazinon degraded significantly faster at low temperatures (4 °C) (Frank et al, 1991) than in groundwater at the same temperature and pH (Druzina and Stegu, 2007), which could be explained by the water quality.

There is also a difference in the degradation rates between river water and filtered river water, with longer persistence determined in unfiltered river water (Lartiges and Garrigues, 1995). As for malathion, the possible explanation can be the adsorption of diazinon on particulates in the river water.

Very fast degradation of diazinon in ultrapure water at low pH (22 °C, pH 6.1, DT_{50} = 6.9) in comparison with degradation in river water at the same temperature and even higher pH (pH 7.3, DT_{50} = 80) suggested that particulates or other dissolved substances can significantly slow down the degradation of diazinon (Lartiges and Garrigues, 1995).

The degradation of diazinon was faster in river water than in ground water (at 25 °C) despite the slightly higher pH in the ground water. The reason might have been the different water quality or microbiological activity (Druzina and Stegu, 2007).

In a study by Bondarenko et al. (2004), several water sources showed different degradation rates. The order of degradation half-lives at 21 °C was: creek water < marsh water < canyon water (with the highest pH) < seawater. At 10 °C, the order was changed: canyon water < creek water < marsh water < seawater, where the half-life in seawater was several times longer than in other water types. Considering water quality, canyon water contained more biological oxygen demand and total organic carbon than any of the other investigated water types, while seawater contained more chlorates and less total suspended solids than other water types, but the highest electrical conductivity (Bondarenko et al., 2004).

When compared to sterile waters, all water sources (creek, marsh, seawater, canyon) showed great difference in the degradation rates in comparison to non-sterile waters, indicating the microbiological activity effect on the diazinon degradation (Bondarenko et al., 2004).

Seasonal changes in river water quality could result in a significant difference in diazinon persistence. The degradation rate in water sampled in August (10 °C, pH 7.3–7.7., DT_{50} = 134 days) was significantly lower than those sampled in April (10 °C, pH 7.9–8.1, DT_{50} = 9 days) (Starner et al., 1999) This observation can be explained by the seasonal change in river water chemistry and microbiological activity.

Finally, it seems that not only pH and temperature of water have influence on the degradation rates of diazinon, but also other water quality parameters such as suspended particulates, water chemistry or microbial capacity.

Chlorpyrifos

Chlorpyrifos shows more rapid hydrolysis under alkaline conditions compared to neutral or acidic conditions (Hui et al., 2010). In a study carried out by Druzina and Stegu (2007), chlorpyrifos showed significant persistence in acidic conditions, making the pH value rise from 6 to 7, a factor very important for the chlorpyrifos degradation rate. Results of the several studies on the degradation of chlorpyrifos in different types of water are summarized in Table 3.

When comparing half-lives in distilled buffered water at 29 °C and pH 4, 7 and 10, it can be noticed that the rate of degradation increased as the pH increased (Hui et al., 2010). The same effect was observed in groundwater at 25 °C and pH 6, 7 and 8.5 (Druzina and Stegu, 2007) as well as in distilled water at 25 °C and pH 4.7, 6.9 and 8.1 (Meikle and Youngson, 1978). In the study by Hui et al. (2010), a temperature increases from 16 °C to 40 °C poorly affected the degradation of chlorpyrifos in distilled buffered water under neutral pH resulting in slightly faster degradation at high temperature.

Table 3. Half-lives of chlorpyrifos in different water types

Water type	Temperature (°C)	pH	Half-life (days)	Reference
Groundwater	4	7	46.2	Druzina and Stegu, 2007
Groundwater	25	6	192.5	Druzina and Stegu, 2007
Groundwater	25	7	49.9	Druzina and Stegu, 2007
Groundwater	25	8.5	44.4	Druzina and Stegu, 2007
River water	4	8	72.9	Druzina and Stegu, 2007
River water	25	8	57.8	Druzina and Stegu, 2007
River water (unaerated)	28.14	8.46	2.5 (59.52 hours)	Thomas and Mansingh, 2002
Sterilized river water (Susquehanna)	n/a	7.93	126	Liu et al. 2001
Sterilized river water (Choptank)	n/a	7.66	56.3	Liu et al. 2001
Sterilized river water (Patuxent)	n/a	8.15	24.4	Liu et al. 2001
Sterilized river water (Pomcoke)	n/a	7.99	26.5	Liu et al. 2001
River water	23	8.05	39.2	Wu, 2000
River water	(–4)–37	8.2–8.5	46-56	Frank et al, 1991
Creek water	10	8.02	18.7	Bondarenko et al., 2004
Creek water	21	8.02	5.5	Bondarenko et al., 2004
Creek water, sterilized	21	8.02	22.1	Bondarenko et al., 2004
Canyon water	10	8.86	22.4	Bondarenko et al., 2004
Canyon water	21	8.86	9.2	Bondarenko et al., 2004
Canyon water sterilized	21	8.86	21.9	Bondarenko et al., 2004
Marsh water	10	8.07	20.5	Bondarenko et al., 2004
Marsh water	21	8.07	6.3	Bondarenko et al., 2004
Marsh water sterilized	21	8.07	24.2	Bondarenko et al., 2004
Canal water for irrigation	25	8	1.5	Meikle and Youngson, 1978
Bay water	10	7.98	49.4	Bondarenko et al., 2004
Bay water	21	7.98	15.2	Bondarenko et al., 2004
Bay water sterilized	21	7.98	23.1	Bondarenko et al., 2004
Brackish water (unaerated)	28.21	8.68	9.66 (231.84 hours)	Thomas and Mansingh, 2002
Tap water (unaerated)	28.18	5.96	16.8 (403.44 hours)	Thomas and Mansingh, 2002
Tap water	4	8–8.2	27	Frank et al, 1991
Tap water	21	8–8.2	4.8	Frank et al, 1991
De–ionized water	n/a	5.72	45.9	Liu et al. 2001

Continued. Table 3.

Water type	Temperature (°C)	pH	Half-life (days)	Reference
Milli–Q water	23	6.5	56.8	Wu, 2000
Sterilized buffered water	40	8	11.2	Noblet, 1997
Distilled water	25	4.7	62.7	Meikle and Youngson, 1978
Distilled water	25	6.9	35.3	Meikle and Youngson, 1978
Distilled water	25	8.1	22.8	Meikle and Youngson, 1978
Distilled buffered water	16	7	12.3	Hui et al., 2010
Distilled buffered water	29	4	14.0	Hui et al., 2010
Distilled buffered water	29	7	11.3	Hui et al., 2010
Reverse osmosis water	29	7	11.9	Hui et al., 2010
Distilled buffered water	29	10	4.5	Hui et al., 2010
Distilled buffered water	40	7	8.12	Hui et al., 2010

The study by Druzina and Stegu (2007) showed that chlorpyrifos was more persistent to degradation at 25 °C than at 4 °C in ground water at pH 7. On the contrary, increased temperature destabilized chlorpyrifos in the creek water, marsh water, canyon water and bay water (Bondarenko et al., 2004), as well as in tap water (Frank et al, 1991).

Since the water temperature did not have the same effect on the rate of degradation in all types of water, it seems that the effect of increased temperature on chlorpyrifos degradation should be considered in relation to water quality.

In Druzina and Stegu (2007), chlorpyrifos was significantly more persistent in river water (despite higher pH) than in ground water at a temperature of 4 °C. The river water had higher electrical conductivity and turbidity, as well as total organic carbon, manganese, nitrites and Coliform bacteria contents than the ground water. Because chlorpyrifos can be adsorbed to soil or sediment particles more strongly than other organophosphorus insecticides, partitioning into sediment moieties may have great impact on pesticide degradation rates (Bondarenko et al., 2004).

Chlorpyrifos was at least stable in the creek water, and the most stable in seawater (Bondarenko et al., 2004). The degradation half-lives followed the order: creek water < marsh water < canyon water < seawater, where the half-life was significantly longer than in other water types. In terms of water quality, seawater contained more chlorates and less total suspended solids than other water types, and low concentrations of organic matter and nitrate as well, but showed the highest electrical conductivity. Longer persistence of chlorpyrifos in seawater could be explained with a lower extent of biodegradation.

Chlorpyrifos persisted longer in brackish water (DT_{50} = 9.66) than in river water (DT_{50} = 2.48) at a temperature of 28.21 °C (Thomas and Mansingh, 2002).

Very slow degradation of chlorpyrifos in distilled water, compared to rapid degradation in canal water for irrigation at the same temperature and pH, also indicated a significant influence of water quality on pesticide degradation rates (Meikle and Youngson, 1978). The half-lives of chlorpyrifos in all of the tested water types (creek, marsh, seawater, canyon water) were significantly higher in sterilized samples than in unsterilized waters, suggesting an influence of microbial activity on the degradation of chlorpyrifos (Bondarenko et al., 2004).

Comparing the studies in distilled buffered water (Hui et al., 2010) and sterilized distilled buffered water (Noblet, 1997) at 40 °C, the chlorpyrifos degradation rate was lower in sterilized distilled alkaline water (pH 8, DT_{50} = 11.2) than in non-sterilized distilled neutral water (pH 7, DT_{50} = 8.12), which indicated the predominant role of biodegradation.

The study of chlorpyrifos degradation in river waters from four locations in Chesapeake Bay showed that chlorpyrifos was the most stable in the Susquehanna River (Liu et al., 2001). The order of degradation half-lives was: Susquehanna > Choptank > Pomcoke > Patuxent. It seems that the narrow pH range of the river samples between 7.66 and 8.15 did not play an important role in different pesticide degradation rates. Susquehanna River had zero salinity and the lowest copper concentration, but almost as a twice as high content of total suspended particles as other rivers, which might have promoted the adsorption of chlorpyrifos and inhibit its degradation. On the contrary, the authors pointed out that most of the chlorpyrifos was not adsorbed, but remained in the aqueous phase and suggested that other factors such as dissolved metal presence could control the degradation rate of chlorpyrifos. According to Hui et al. (2010), the aqueous hydrolysis of chlorpyrifos may be catalysed by dissolved copper ions. Blanchet and St-George (1982) reported that the rate of hydrolysis of chlorpyrifos could increase, followed by the increase of copper (II) concentration.

Comparing the stability of chlorpyrifos in tap water (Frank et al, 1991) and in other water types such as distilled water (Meikle and Youngson, 1978), river water (Wu, 2000), bay water (Bondarenko et al., 2004) and ground water (Druzina and Stegu, 2007) under similar pH and temperature conditions, it can be noticed that chlorpyrifos degraded more quickly in tap water, probably catalysed by the free chlorine (Duirk and Collette, 2006; Hui et al., 2010).

Stability of organophosphorus pesticides in different water types

The stability of malathion in aqueous solution strongly depends on its temperature and pH. Malathion can be rapidly decomposed in alkaline water. Although water quality also takes some part in malathion hydrolysis, it is more important to maintain the spray solution at a low temperature (4 °C) and in acidic conditions to preserve its application efficiency. Regarding water type, malathion seems to be more stable in soft water. In case of natural water-based sprays that are mostly alkaline, at 20 °C malathion will degrade within several days, but at low temperatures (below 6 °C) it may persist for a few weeks.

Chlorpyrifos is the most stable in acidic aqueous solutions, therefore it is more important to have a spray solution below pH 7 than to keep it at low temperatures. The temperature effect could be pronounced in natural water or tap water types. Chlorpyrifos hydrolysis could be much faster in tap water than in ground water, which can be a suitable choice of water for pesticide spray preparation. Regarding the river type of water, it is likely that chlorpyrifos can be adsorbed by suspended particles, therefore it will be more stable in river water with a high content of total suspended solids. If not used immediately, a chlorpyrifos spray solution should be buffered at pH 6 and kept at low temperature to prevent the effect of biodegradation. If chlorpyrifos reaches natural waters by run off or drift, its degradation may last from several days to several weeks, depending on pH and water quality.

Diazinon is more resilient to alkaline conditions than the other pesticides which mentioned herein, but it is the least resistant to acidic conditions which accelerate its degradation. Temperature can significantly foster or demote the diazinon degradation rate, depending on the water quality. At higher temperatures (above 22 °C), biodegradation can reduce the content of diazinon in several days. By cooling the temperature at 6 °C and buffering the solution to pH 7-8, the stability of diazinon can be prolonged for several days. If reaches natural waters by run off or drift, its degradation may last from several days to several months, depending mostly on pH and temperature, but other water quality parameters cannot be excluded.

CONCLUSIONS

Studies have clearly confirmed the major role of pH and temperature in the degradation of organophosphorus pesticides in water, but only indicated that other water quality parameters also take the part in pesticide stability estimations. The relation between water type and pesticide degradation rate could explain the pesticide efficacy variations at regional level and highlight the pesticide responses to water type. Knowledge of pesticide stability in different water types can also be used in the remediation assessment studies of aquatic ecosystem contaminated with organophosphorus pesticide residues.

If not used immediately after spray preparation, the enhanced degradation of the active substance in the tank should be avoided by keeping the spray solution at thermostated and buffered conditions.

Considering that water type can affect the stability of susceptible pesticides, the effect of water composition and other related properties such as alkalinity, hardness, salinity, turbidity, electrical conductivity, contents of the total suspended solids and total dissolved substances on the pesticide degradation should be further explored to provide the optimal efficiency of pesticide application.

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