

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

**Geographical and temporal assessment of the photochemical decontamination potential of river waters from agrochemicals: A first application to the Piedmont region (NW Italy)**

**This is the author's manuscript**

*Original Citation:*

*Availability:*

This version is available <http://hdl.handle.net/2318/1772472> since 2021-02-11T12:54:18Z

*Published version:*

DOI:10.1016/j.chemosphere.2020.127921

*Terms of use:*

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

# **Geographical and temporal assessment of the photochemical decontamination potential of river waters from agrochemicals: A first application to the Piedmont region (NW Italy)**

**Luca Carena, Silvia Comis, Davide Vione \***

*Department of Chemistry, University of Torino, Via Pietro Giuria 5, 10125 Torino, Italy.*

\* Corresponding author. E-mail: *davide.vione@unito.it*

## ***Abstract***

This work shows the potential of using photochemical modelling to assess the river-water ability to photodegrade agrochemicals on a geographic and temporal scale. The case of flowing water requires different data treatment compared to more stationary water bodies (*e.g.*, lakes), but it could allow for the identification of particularly vulnerable environments. Five pesticides were considered here, and the photodegradation rate followed the order bentazon > isoproturon > dimethomorph ~ chlortoluron > atrazine. The modelled photodegradation kinetics was particularly fast in the river Po, which receives significant input of agricultural nitrate from groundwater and features higher steady-state [ $\bullet\text{OH}$ ] than most other rivers in the region. The fact that the Po eventually collects all river waters in Piedmont is positive, from the point of view of comprehensive photodegradation of pesticides. However, this paradoxical situation of agricultural pollution (nitrate) helping fight pollution from the same source (pesticides) has two important limitations: (i) compared to the parent compounds, some intermediates deriving from  $\bullet\text{OH}$  reactions are either more harmful (N-formyl derivatives of phenylureas), or about as harmful (desethyl atrazine); (ii) banned atrazine is no longer sprayed over fields during the plant growth season, but it reaches surface waters from legacy groundwater inputs. The latter are operational also during winter, when photochemistry is least active. Therefore, photochemistry might not ensure considerable attenuation of atrazine during

wintertime. Overall, bentazon would be the safest among the studied pesticides because of fast degradation by direct photolysis, and of low ecotoxicological impact of its phototransformation intermediates.

**Keywords:** Direct photolysis; Hydroxyl radicals; Nitrate contamination; Pesticides; Phenylureas; Bentazon; Atrazine.

## 1. Introduction

Pollution by pesticides affects both surface waters and groundwater around the world. It is a considerable problem for both aquatic organisms and the protection of water resources, *e.g.*, drinking water (Song et al., 2010). A considerable difficulty with agricultural pollution is that it is made up of a multitude of non-point sources (Ongley et al., 2010), which are more difficult to control and treat compared to point sources such as urban wastewaters. Both cases are presently very problematic but, if wastewaters are often incompletely treated for emerging pollutants (Castiglioni et al., 2006; Richardson and Ternes, 2014), agricultural runoff is usually non-treated at all. The situation would be even worse, were it not for the self-depuration ability of natural waters. In particular, pesticides in surface waters undergo both bio- and photodegradation as important natural attenuation processes (Fenner et al., 2013). As far as phototransformation is concerned, it is usually divided into direct photolysis and indirect photochemistry. In the former, the pesticide absorbs sunlight and gets transformed through different pathways (*e.g.*, bond breaking, ionisation, excited-state reactions) (Pace and Barreca, 2014). In the case of indirect phototransformation, sunlight is absorbed by natural water components such as chromophoric dissolved organic matter (CDOM) and nitrate, to produce a range of PPRIs (photochemically produced reactive intermediates) (Rosario-Ortiz and Canonica, 2016). Important PPRI in surface waters are the hydroxyl ( $\bullet\text{OH}$ ) and carbonate ( $\text{CO}_3^{\bullet-}$ ) radicals, CDOM triplet states ( $^3\text{CDOM}^*$ ) and singlet oxygen

( $^1\text{O}_2$ ), which are involved in pollutant degradation (Remucal, 2014). These PPRIs are produced in sunlit surface waters but are also scavenged/quenched very fast by dissolved organic matter ( $\bullet\text{OH}$ ,  $\text{CO}_3^{\bullet-}$ ), inorganic carbon ( $\bullet\text{OH}$ ),  $\text{O}_2$  or internal conversion ( $^3\text{CDOM}^*$ ), and collision with water ( $^1\text{O}_2$ ) (Vione et al., 2014; McNeill and Canonica, 2016). Because of this formation/consumption budget, PPRIs reach steady-state concentration values that are usually very low ( $10^{-17}$  mol L $^{-1}$  for  $\bullet\text{OH}$ ,  $10^{-16}$ - $10^{-14}$  mol L $^{-1}$  for  $\text{CO}_3^{\bullet-}$ ,  $10^{-16}$ - $10^{-15}$  mol L $^{-1}$  for  $^3\text{CDOM}^*$  and  $^1\text{O}_2$ ) (Vione et al., 2014). Recently, it has become possible to reliably model the photochemical reaction kinetics of pollutants in surface waters based on the photochemical reactivity parameters of the pollutants themselves (absorption spectrum, direct photolysis quantum yield, second-order reaction rate constants with PPRIs), and on environmental parameters such as sunlight irradiance and spectrum, water depth and chemistry (Carena et al., 2019; Parizi et al., 2019). Photochemical modelling yields the pseudo-first order degradation rate constants of pollutants and their corresponding half-life times, as well as the prevailing photodegradation pathway(s) (direct photolysis or reaction with one or more PPRIs) (Zhou et al., 2018; Vione, 2020). In the case of flowing aquatic systems such as rivers and streams, the photochemical lifetimes of pollutants should be compared with the in-stream residence time of water, to see whether photodegradation may be an important attenuation pathway (Fono et al., 2006; Vione et al., 2018).

Environmental databases often contain time series of water chemistry data that can be exploited for photochemical modelling (Minella et al., 2016). In fortunate cases the data may be extended over both space and time, thereby allowing for the assessment of the time evolution of photochemistry in large geographic regions. An advantage of the geographical approach is the possibility to find out potentially vulnerable environments (Carena and Vione, 2020). To our knowledge, the combination of space and time series has hardly been exploited in photochemical modelling. In this work we provide a proof-of-concept of how this approach could be carried out. The photodegradation kinetics of five pesticides occurring in the Piedmont region (NW Italy) is here modelled over space and time. The choice of the pesticides (atrazine, ATZ; bentazon, BTZ; chlortoluron, CTL;

dimethomorph, DMM; isoproturon, IPT) was made by crossing their occurrence in Piedmont (ARPA, 2020), with the availability of photoreactivity data that enable modelling (Vione, 2020). The results allow for an assessment of the potential of Piedmont's river waters to induce the natural photochemical attenuation of a range of occurring pesticides, as well as for seeing which of them might pose the highest (or the lowest) environmental concern.

## 2. Methods

### 2.1. Source data

The water chemistry data used in this work were provided by the regional environmental protection agency (ARPA Piemonte; ARPA, 2020). The data are not directly available on the agency's website, but they are provided on request. They include the time series of the main water parameters, such as those of photochemical significance (nitrate, organic matter, inorganic carbon species), and the concentration values of a wide range of pollutants that are routinely monitored. The 2000-2008 time series was the most complete as it complied with EU legislation requirements to assess the ecological status of rivers (Achleitner et al., 2005), thus each site was sampled once a month. Because rivers having a good status could be sampled less frequently after 2008, more recent data were less suitable to derive year-round averages of photochemical reactivity. For this reason, river-water photochemistry is here modelled for the years 2000-2008.

### 2.2. Studied pesticides

The pesticides to be studied were chosen based on two parameters: (i) actual occurrence in surface waters in the Piedmont region, and (ii) availability of photodegradation kinetics data (absorption spectrum, direct photolysis quantum yield, second-order reaction rate constants with the PPRIs  $\cdot\text{OH}$ ,  $\text{CO}_3^{\cdot-}$ ,  $^1\text{O}_2$  and  $^3\text{CDOM}^*$ ). By crossing the two datasets, photodegradation kinetics was

studied for the following five pesticides: atrazine, bentazon, chlortoluron, dimethomorph and isoproturon. Pesticide occurrence in Piedmont (ARPA, 2020) is reported in **Figure 1**. Each symbol means that the given pesticide was detected at least once in the relevant site. However, in **Figure 1a** the samples referring to isoproturon, chlortoluron and dimethomorph were mostly below the quantification limit (ARPA, 2020).

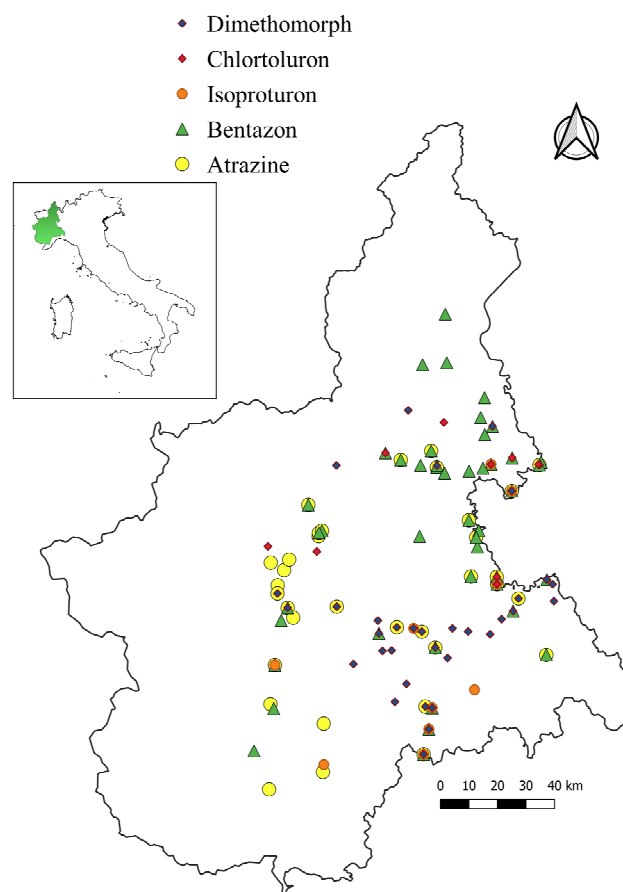
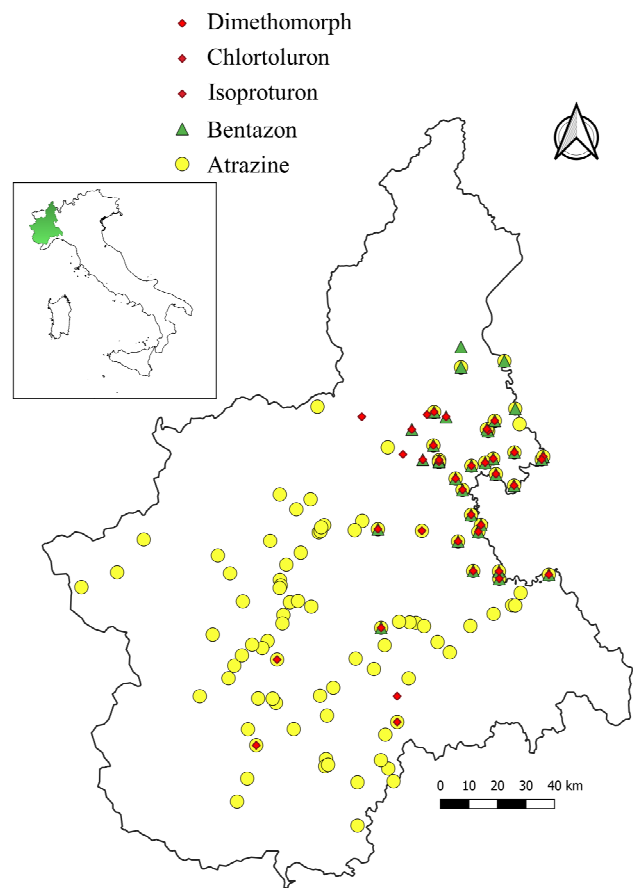
Note the widespread distribution of atrazine in Piedmont's surface waters in 2000-2008 (**Figure 1a**), at which time atrazine had already been banned and was no longer used. The likely reason is the persistence of this compound in groundwater (Silva et al., 2012), from which it can reach surface waters, and the relatively few years that had passed since its ban. Indeed, a decrease in the geographical distribution of atrazine was observed in 2009-2014 (**Figure 1b**) compared to 2000-2008. The opposite phenomenon is seen for the other pesticides, which might suggest a gradual replacement in used agrochemicals.

The photoreactivity data of the studied pesticides are reported in **Table 1**. Their absorption spectra are shown in **Figure S1** of the Supplementary Material (hereinafter, SM). Note that BTZ has a strong absorption band in the UVB-UVA region (Carena et al., 2020); therefore, it is the studied pesticide that undergoes direct photolysis to the highest extent, despite the fact that it has the second-lowest quantum yield of direct photolysis.

1

(a) 2000-2008

(b) 2009-2014



2

3

4 **Figure 1.** Geographical distribution of the five pesticides under study in the Piedmont region, in the years (a) 2000-2008 and (b) 2009-2014. The  
 5 pesticides dimethomorph, chlortoluron and isoproturon were actually below the quantification limit in most sampling sites in 2000-2008.

**Table 1.** *Upper panel:* photoreactivity data of the studied pesticides (direct photolysis quantum yield  $\Phi$ , second-order reaction rate constants with the PPRIs  $\bullet\text{OH}$ ,  $\text{CO}_3^{\bullet-}$ ,  $^1\text{O}_2$  and  $^3\text{CDOM}^*$ ). *Lower panel:* main photodegradation pathways of the studied pesticides in natural surface waters (d.p. = direct photolysis). (Marchetti et al., 2013; Avetta et al., 2014; Fabbri et al., 2015; Carena et al., 2020).

Pesticide	Acronym	$\Phi$ , unitless	$k_{P+\bullet\text{OH}}$ , L $\text{mol}^{-1} \text{s}^{-1}$	$k_{P+\text{CO}_3^{\bullet-}}$ , L $\text{mol}^{-1} \text{s}^{-1}$	$k_{P+^1\text{O}_2}$ , L $\text{mol}^{-1} \text{s}^{-1}$	$k_{P+^3\text{CDOM}^*}$ , L $\text{mol}^{-1} \text{s}^{-1}$
Atrazine	ATZ	$1.6 \times 10^{-2}$	$2.7 \times 10^9$	$4 \times 10^6$	Negligible	$7.2 \times 10^8$
Bentazon	BTZ	$4.4 \times 10^{-4}$	$5.7 \times 10^9$	$2.5 \times 10^7$	$3.1 \times 10^7$	$9.7 \times 10^8$
Chlortoluron	CTL	$3 \times 10^{-2}$	$6.9 \times 10^9$	$1.7 \times 10^7$	Negligible	$2.7 \times 10^9$
Dimethomorph	DMM	$2.6 \times 10^{-5}$	$2.6 \times 10^{10}$	Negligible	$8.5 \times 10^5$	$1.6 \times 10^9$
Isoproturon	IPT	$2 \times 10^{-3}$	$7.9 \times 10^9$	$3 \times 10^7$	Negligible	$3.2 \times 10^9$
Pesticide use			Main photodegr. pathway(s)			
Atrazine	ATZ	Herbicide (maize, banned)	$\bullet\text{OH}$ , $\text{CO}_3^{\bullet-}$ , $^3\text{CDOM}^*$ , d.p.			
Bentazon	BTZ	Herbicide	d.p.			
Chlortoluron	CTL	Herbicide (cereals)	$\bullet\text{OH}$ , $\text{CO}_3^{\bullet-}$ , $^3\text{CDOM}^*$ , d.p.			
Dimethomorph	DMM	Fungicide	$\bullet\text{OH}$ , $^3\text{CDOM}^*$			
Isoproturon	IPT	Herbicide (cereals)	$\bullet\text{OH}$ , $\text{CO}_3^{\bullet-}$ , $^3\text{CDOM}^*$			



### 2.3. The photochemical model

The photochemical half-life time ( $t_{1/2}$ , days) of the selected pesticides was calculated for each month from their overall degradation rate constants ( $k'_{tot}$ ), which consider both direct and indirect photochemistry (Bodrato and Vione, 2014).

$$t_{1/2} = \frac{\ln 2}{k'_{tot}} \quad (1)$$

$$k'_{tot} = k'_{d,p} + \sum_i k_{(p+i)} [i] \quad (2)$$

In **Equation (2)**,  $[i]$  (mol L<sup>-1</sup> units) is the steady-state concentration of the PPRI  $i$  ( $i = \cdot\text{OH}$ ,  $\text{CO}_3^{\cdot-}$ ,  $^1\text{O}_2$ , or  $^3\text{CDOM}^*$ ), while  $k_{(p+i)}$  (L mol<sup>-1</sup> s<sup>-1</sup>) is the second-order rate constant for the reaction of  $i$  with the pesticide  $P$  (see **Table 1**). The detailed procedure for the determination of  $[i]$  is explained in **Text S1(SM)**. The direct photolysis rate constant ( $k'_{d,p}$ , s<sup>-1</sup>) was assessed by multiplying the polychromatic apparent quantum yield of the pesticide direct photolysis ( $\Phi_P$ , unitless) by the photon-absorption rate constant of the pesticide itself ( $P'_{a,P}$ , units of s<sup>-1</sup>):  $k'_{d,p} = \Phi_P P'_{a,P}$  (Braslavsky, 2007).

$P'_{a,P}$  was calculated as the numerical integral over wavelength of the rate constant of spectral photon absorption of each pesticide ( $p'_{a,p}(\lambda)$ , units of s<sup>-1</sup> nm<sup>-1</sup>). Numerical integration was carried out over the wavelength range where the spectrum of incident sunlight ( $p^0(\lambda)$ , vide infra) and the absorption spectrum of the pesticide overlap, using the trapezoidal rule (Bodrato and Vione, 2014):

$$P'_{a,P} = \sum_i (\lambda_i - \lambda_{i-1}) \frac{p'_{a,p}(\lambda_i) + p'_{a,p}(\lambda_{i-1})}{2} \quad (3)$$

The value of  $p'_{a,p}(\lambda)$  was calculated as follows:

$$p'_{a,p}(\lambda) = p^0(\lambda) \frac{\varepsilon_p(\lambda)}{DOC A_1(\lambda)} [1 - 10^{-d DOC A_1(\lambda)}] \quad (4)$$

where:  $p^0(\lambda)$  is the mid-latitude spectral photon flux density of sunlight (mol of photons  $L^{-1} s^{-1}$ ) that reaches the ground at noon  $\pm 3$  h on the 15<sup>th</sup> day of the given month (it is a reasonable approximation of the solar spectrum averaged over the daytime hours) (Bodrato and Vione, 2014);  $\epsilon_p(\lambda)$  is the molar absorption coefficient of the pesticide at the wavelength  $\lambda$  ( $L mol^{-1} cm^{-1}$ ); DOC is the dissolved organic carbon ( $mg_C L^{-1}$ );  $A_1(\lambda)$  ( $L mg_C^{-1} cm^{-1}$ ) is the specific CDOM absorbance at the wavelength  $\lambda$ , over an optical path length of 1 cm ( $A_1(\lambda, nm) = 0.45 \exp(-0.015\lambda)$ ) (Vione et al., 2010); finally,  $d$  is the optical path of radiation in the water column. In particular,  $d$  takes into account the monthly variation of the solar zenith angle (Bodrato and Vione, 2014). Considering that water in many rivers is quite shallow, we used here  $d = 50$  cm.

The obtained monthly values of  $k'_{tot}$  ( $s^{-1}$ ) were then converted into  $day^{-1}$  units by considering the number of hours of solar irradiation for each month at 45°N – 7°E (9 hours for December and January, 10.5 for February, 12 for March, 13.5 for April, 15 for May, 16 for June, 15.5 for July, 14.3 for August, 12.5 for September, 11 for October, and 9.5 for November; NCAR, 2020). Finally, the photochemical half-life time (days) for each month was calculated as  $t_{1/2} = \ln 2 (k'_{tot})^{-1}$ .

Previous studies have shown that the described approach is able to predict quite well the lifetimes of ATZ (McConnell et al., 2004; Chung and Gu, 2009; Marchetti et al., 2013), BTZ (Al Housari et al., 2011; Carena et al., 2020) and several phenylurea herbicides (Gerecke et al., 2001; Fabbri et al., 2015) in surface waters.

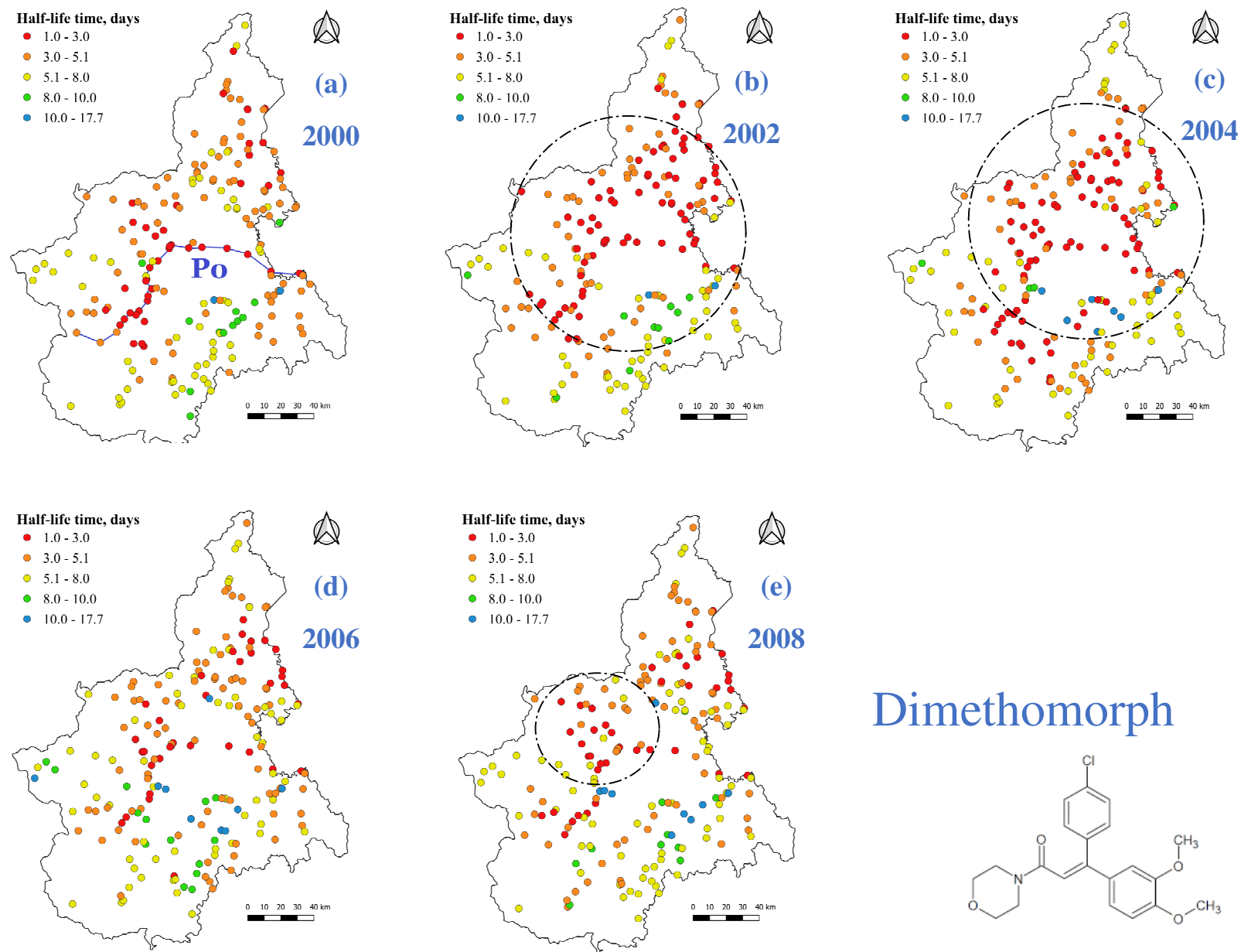
Statistical analysis was performed with both Excel and QGIS software. Mapping was carried out with the QGIS software version 3.2.2 ‘Bonn’ (QGIS, 2020).

### 3. Results and Discussion

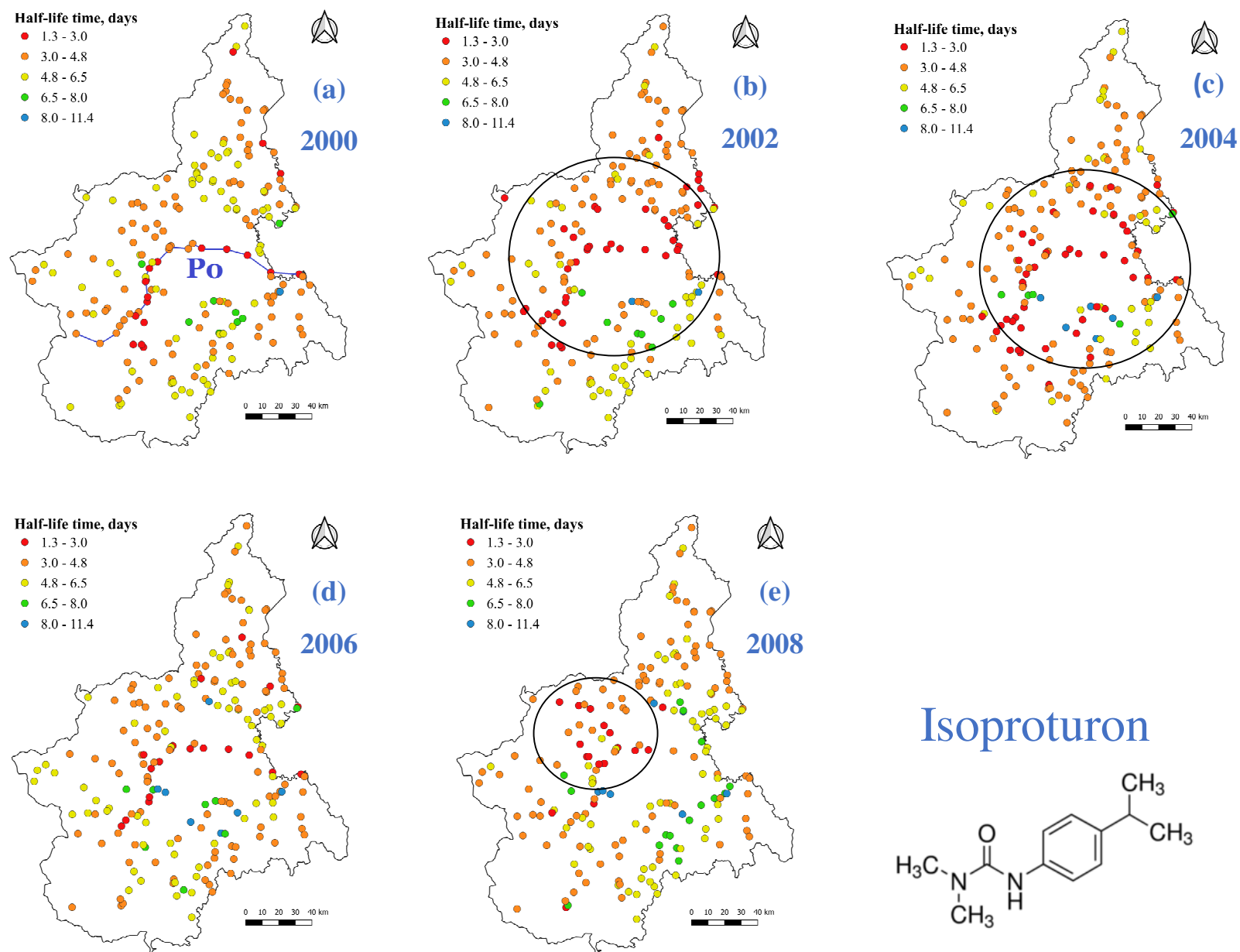
#### 3.1. Assessment of surface-water photochemistry over space and time

The kinetic model yielded the steady-state concentration values of  $\bullet\text{OH}$  (**Figure S2(SM)**),  $\text{CO}_3^{\bullet-}$  (**Figure S3(SM)**) and  $^3\text{CDOM}^*$  (**Figure S4(SM)**), as year averages at each sampling point (note that  $[\text{}^1\text{O}_2] \sim [^3\text{CDOM}^*]$ ). These values were used in **Equation (2)** to derive the pseudo-first-order degradation rate constants of the pesticides, as well as the corresponding half-life times by means of **Equation (1)**. The lifetime maps are reported for ATZ (**Figure S5(SM)**), BTZ (**Figure S6(SM)**), CTL (**Figure S7(SM)**), DMM (**Figure 2**) and IPT (**Figure 3**).

In the case of DMM and IPT, it is interesting to observe that photodegradation was generally faster in the central part of the region in 2002 and 2004 (see the highlighted parts of the map in panels (b,c) of **Figures 2,3**). A similar issue was also observed for ATZ and CTL, but not for BTZ. The main difference is that BTZ undergoes photodegradation mainly by direct photolysis (Carena et al., 2020), while the indirect photodegradation by  $\bullet\text{OH}$ ,  $\text{CO}_3^{\bullet-}$  and  $^3\text{CDOM}^*$  is additionally important in the case of the other compounds (**Table 1**). In particular, in the highlighted zone one has higher steady-state  $[\bullet\text{OH}]$  and  $[\text{CO}_3^{\bullet-}]$  in 2002 and 2004 compared to the other years (**Figures S2,S3(SM)**), which could account for faster photodegradation in 2002 and 2004. Higher  $[\bullet\text{OH}]$  and  $[\text{CO}_3^{\bullet-}]$  could be due to more concentrated sources (*e.g.*  $\text{NO}_3^-$ , which photoproduces  $\bullet\text{OH}$  directly and  $\text{CO}_3^{\bullet-}$  indirectly, upon oxidation of inorganic carbon by  $\bullet\text{OH}$ ) or less concentrated sinks (mostly dissolved organic matter, DOM, which is measured as the DOC) (Brezonik and Fulkerson-Brekken, 1998). A mixed explanation holds here: lower DOC in 2002-2004 compared to 2000 (see **Figure S8(SM)**) could account for the correspondingly higher  $[\bullet\text{OH}]$  and  $[\text{CO}_3^{\bullet-}]$  in 2002-2004, but the DOC could not explain the differences between 2002-2004 and 2006-2008. In the latter case, enhanced photodegradation in 2002-2004 is accounted for by higher nitrate.



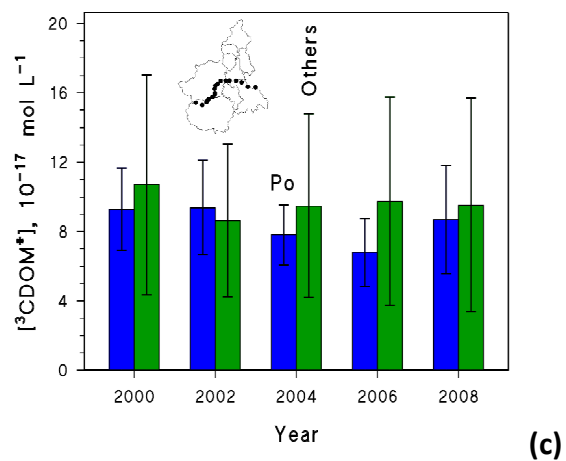
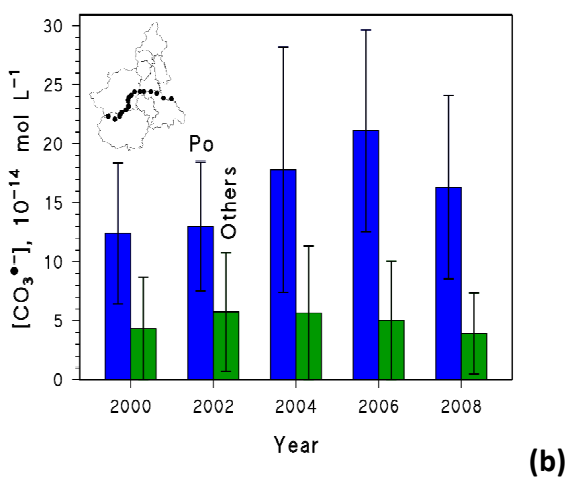
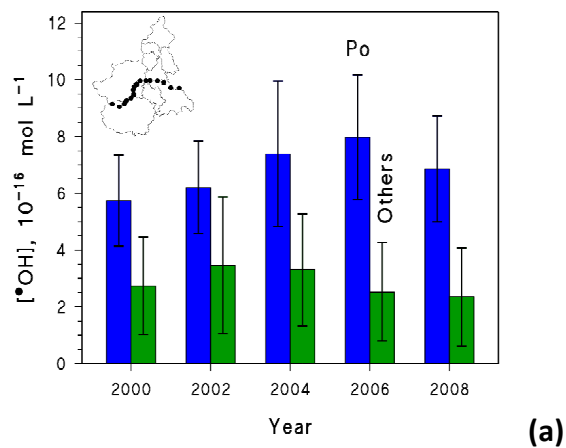
**Figure 2.** Photochemical maps of Piedmont over the years 2000-2008, showing the half-life times of DMM (year-round averages) in the different sampling points. The connecting lines in panel (a) highlight the course of the Po river, the main watercourse of Piedmont and of Italy as well. The circles in panels (b,c) highlight the zones where photodegradation was peculiarly fast (for DMM, as well as for the other pesticides except BTZ) in 2002 and 2004. Similar issue holds for the circle in panel (e), but in this case the photodegradation was fast for BTZ as well.



**Figure 3.** Photochemical maps of Piedmont over the years 2000-2008, showing the half-life times of IPT (year-round averages) in the different sampling points. The connecting lines in panel (a) highlight the course of the Po river, the main watercourse of Piedmont and of Italy as well. The circles in panels (b,c) highlight the zones where photodegradation was peculiarly fast (for IPT, as well as for the other pesticides except BTZ) in 2002 and 2004. Similar issue holds for the circle in panel (e), but in this case the photodegradation was fast for BTZ as well.

Faster photodegradation in the central part of the region in 2002 and 2004 would be particularly significant, because this is the zone where the occurrence of pesticides is the highest (see **Figure 1**). Another interesting issue is that the photodegradation of all the compounds, including BTZ, was peculiarly fast in a limited part of the region during the year 2008. The relevant locations are highlighted in panels (e) of **Figures 2,3**. The phenomenon is particularly evident for ATZ, BTZ, CTL and IPT, and a bit less for DMM. The zone is characterized by quite low DOC values (around  $0.5\text{--}1.0\text{ mg}_C\text{ L}^{-1}$ , see **Figure S8(SM)**), thus one can exclude an important contribution of photoprocesses triggered by  $^3\text{CDOM}^*$  and  $^1\text{O}_2$  (see **Figure S9(SM)** for a trend of the steady-state concentrations of PPRI as a function of the DOC). In contrast, reactions induced by  $^{\bullet}\text{OH}$ ,  $\text{CO}_3^{\bullet-}$  and the direct photolysis could play important roles in DOM-poor waters (Vione et al., 2014). There was nothing peculiar about the steady-state  $[\text{CO}_3^{\bullet-}]$  in the relevant locations in 2008, while  $[^{\bullet}\text{OH}]$  was a bit higher than the regional average but could not account alone for the observed kinetics (**Figures S2, S3(SM)**). Fast BTZ photodegradation suggests that water conditions were favourable to the direct photolysis process. Direct photolysis can be inhibited by CDOM that competes with the pollutants for sunlight irradiance (Vione et al., 2014). Moreover, photolysis is a secondary pathway for DMM, which could explain why the trend was less marked for this compound. A likely explanation is connected to the peculiarly low values of the DOC (and of CDOM as a consequence) in the zone of interest in 2008, which would enhance the direct photolysis processes (see **Figure S10(SM)** for a detailed DOC map of Piedmont in 2008, which highlights this issue).

There was also an interesting difference in photodegradation kinetics between the river Po and the other watercourses of the region. The lines in panel (a) of **Figures 2,3** highlight the course of the Po river, which is the main watercourse in Piedmont as well as the longest in Italy (650 km, flowing in four Italian regions till the Adriatic Sea). Compared to the other rivers and streams of Piedmont, the Po had higher levels of both  $^{\bullet}\text{OH}$  and  $\text{CO}_3^{\bullet-}$  (see **Figure 4**, as well as **Figures S2, S3(SM)**).



**Figure 4.** Annual averages of the steady-state concentration of  $\bullet\text{OH}$  (a),  $\text{CO}_3^{\bullet-}$  (b) and  $^3\text{CDOM}^*$  (c) in the river Po (blue bars), and all the other rivers of Piedmont (green bars). The associated variability is the spatial standard deviation. The insets show the Piedmont map with the relevant administrative boundaries (provinces), and the data points along the river Po. Differences are statistically significant at  $\alpha = 0.05$  (t-test for paired data) for (a) and (b), and insignificant for (c).

In contrast, no significant difference between the Po and other watercourses could be detected in the case of  $^3\text{CDOM}^*$ . The peculiarly high values of  $[\bullet\text{OH}]$  and  $[\text{CO}_3^{\bullet-}]$  in the Po compared to the other rivers and streams of the region are caused by high nitrate levels (see **Figure S11(SM)**). Indeed, no statistically significant differences could be found for the DOC, which is the additional main parameter that affects  $[\bullet\text{OH}]$  and  $[\text{CO}_3^{\bullet-}]$  (Brezonik and Fulkerson-Brekken, 1998).

The elevated nitrate concentration in the Po river is accounted for by the interaction of its surface waters with groundwater of the surrounding plain. Previous studies have shown that the river Po, after it leaves the uplands and enters the plain, behaves as a ‘gaining stream’ by receiving water supply from surrounding groundwater (Lasagna et al., 2016a). The hydraulic gradient is higher near the Alps and decreases in the lower plain towards the Po, thus aquifers can flow from the Alps to the river by passing through the plain, which is mainly characterized by soils with high permeability (Lasagna et al., 2016a, 2016b; Martinelli et al., 2018). One of the important anthropogenic impacts in this area is the contamination of shallow aquifers by nitrate, due to the high use of N-based fertilizers and zootechnical effluents in agricultural activities (Franchino et al., 2014; Lasagna and De Luca, 2019). The concentration values of nitrate in aquifers in the investigated period usually ranged from some tens to  $\sim 100 \text{ mg L}^{-1}$ , with locally high contamination of up to  $\sim 300 \text{ mg L}^{-1}$  (Bassanino et al., 2011; Debernardi et al., 2008; Lasagna et al., 2016a; Martinelli et al., 2018). Furthermore, nitrogen inputs to aquifers from agricultural activities are higher in the lower plain than near the Alps (Bassanino et al., 2011). As a consequence, one observes a gradual increase of nitrate concentration values in both ground- and surface waters when going from the Alps to the lower plain, and shallow aquifers in the plain can discharge nitrate into the Po river (Lasagna et al., 2016a). Although nitrate concentrations are generally lower in rivers than in groundwater because of denitrification and dilution processes taking place in the riparian and hyporheic areas (Lasagna et al., 2016b), watercourses affected by nitrate-contaminated groundwater are understandably more nitrate-rich than non-affected ones.

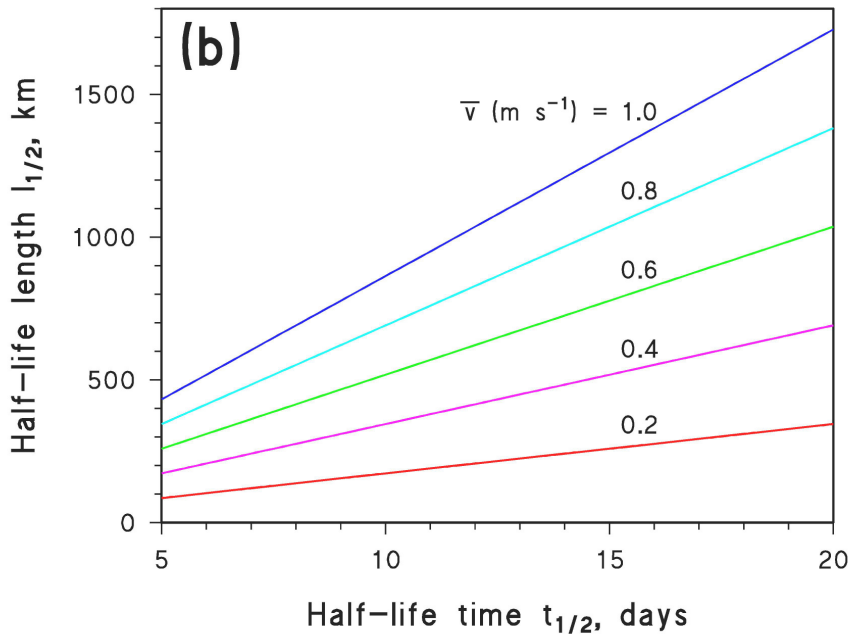
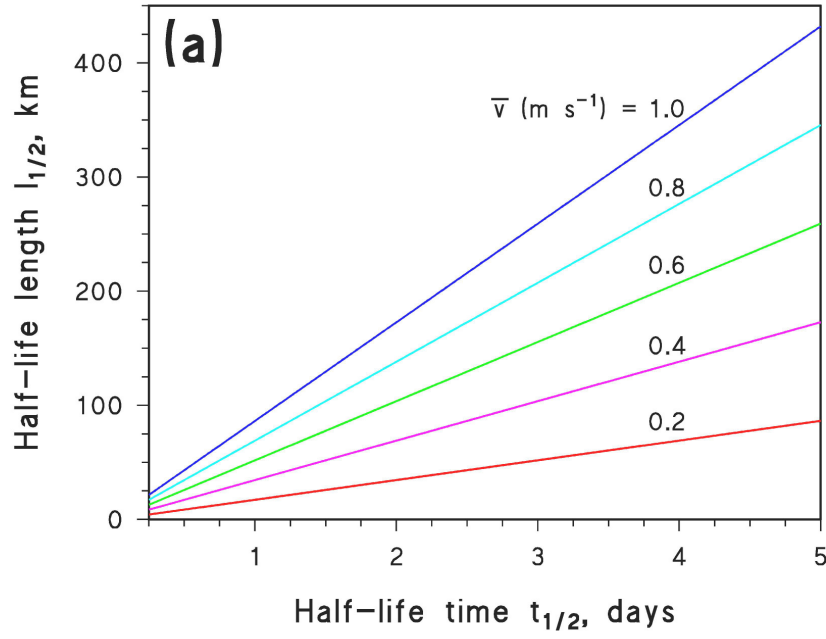


Groundwater contamination by nitrate due to agricultural activities, followed by aquifer discharge into surface waters is a good example of how anthropogenic activities can impact the photochemistry of surface waters. Surface-water contamination by pesticides is another impact of agricultural activities: in this case the two effects would partially cancel out because of  $\bullet\text{OH}$  photoproduction by nitrate, which aids photochemical depollution.

### ***3.2. Environmental implications of the modelled photodegradation kinetics***

Pesticide lifetimes in different sampling points ranged from less than one day to some weeks; the degradation rate constants generally followed the order  $\text{BTZ} > \text{IPT} > \text{CTL} \sim \text{DMM} > \text{ATZ}$ . However, lifetimes should be set in the context of flowing river water (Vione et al., 2018). Differently from stationary water systems such as lakes, where water can have quite long residence times, the time scales of river photochemistry are considerably shorter. In addition to lifetimes, it is thus important to have insight into the half-life lengths ( $l_{1/2}$ ) of pollutants in rivers (Vione and Scozzaro, 2019). A half-life length is the length of the sunlit river-stretch that is required to halve the pollutant concentration, in this case due to photochemical degradation processes. The lower is  $l_{1/2}$ , the higher is the probability that a pollutant undergoes effective photodegradation in river water. It is  $l_{1/2} = \bar{v} t_{1/2}$ , where  $\bar{v}$  is the average water flow velocity. The value of  $\bar{v}$  under normal flow conditions in lowland rivers can be around  $1 \text{ m s}^{-1}$ , but  $\bar{v}$  can be considerably lower during water scarcity or drought periods (Godinho et al., 2000; Kilsby et al., 2007; Barbosa et al., 2010). Indeed, photodegradation processes in river water are most efficient during droughts, and can be negligible during floods (Vione and Scozzaro, 2019).

The trend of  $l_{1/2}$  as a function of  $\bar{v}$  and  $t_{1/2}$  is reported in **Figure 5**. The half-life length is often longer than the distance between two sampling points, thus the average values of  $t_{1/2}$  and  $\bar{v}$  along a river course should be considered.



**Figure 5.** Trends of the half-life lengths  $l_{1/2}$  of a generic pollutant in a river course, as a function of the (average) half-life time  $t_{1/2}$  and for different values of the (average) water flow velocity  $\bar{v}$ . The  $t_{1/2}$  range found for the different pesticides (0.5-20 days) is here split into two parts for ease of readability, namely 0.25-5 days (**panel a**) and 5-20 days (**panel b**).

Given the  $t_{1/2}$  values and the typical lengths of rivers and streams within the regional borders of Piedmont, effective pesticide photodegradation is highly likely if  $t_{1/2} < 2$  days, almost irrespective of the flow conditions (floods would be an exception, because  $\bar{v} \gg 1 \text{ m s}^{-1}$ ; Vione and Scozzaro, 2019). In contrast, photodegradation would be minor to negligible if  $t_{1/2} > 5$  days, unless severe water scarcity is operational.

It should be noted that all watercourses in Piedmont end up in the Po river, where photoactivity is higher than average. Therefore, in several cases photodegradation could be slow in the initial tract but would then accelerate once the main river is reached. Therefore, the nitrate-rich Po waters would play a key role in collecting water-carried pesticides and ensuring their effective photoinduced degradation.

The above scenario has two caveats, however. The first is that photochemical degradation may produce harmful intermediates. Given the features of the regional waters and of the studied pesticides, the  $\bullet\text{OH}$  reactions are particularly relevant with the single exception of BTZ. Although fast BTZ photodegradation by direct photolysis would produce effective decontamination (Carena et al., 2020), phenylurea herbicides such as CTL and IPT are known to produce toxic N-formyl compounds upon reaction with  $\bullet\text{OH}$  (Galichet et al., 2002; Poulain et al., 2003; Halladja et al., 2007; Shankar et al., 2008). Moreover, the reaction of ATZ +  $\bullet\text{OH}$  yields desethyl atrazine with high yield, and the two compounds have comparable environmental effects (Marchetti et al., 2013). Therefore, in several cases complete decontamination by photochemical processes would take longer time than the mere disappearance of the parent compound. From this point of view, BTZ appears to be the safest pesticide among those under study. The second caveat is that the reported lifetimes are year averages, and actual photodegradation would be considerably faster in spring-summer and considerably slower in autumn-winter. Pesticides are usually not sprayed during wintertime, but ATZ (the most stable pesticide among those under study) is for instance no longer used and it reaches surface waters only through groundwater inputs (Silva et al., 2012). Gradual leaching of the groundwater ATZ reservoir to surface waters would not stop in winter, when poor

water photoreactivity combined with the relative stability of ATZ might not ensure effective degradation.

## 4. Conclusions

The mapping of river-water photoreactivity in the Piedmont region (NW Italy) suggests that some parts of the region showed high ability to photodegrade pollutants in peculiar years, mostly due to nitrate increase and (sometimes) decrease of the DOC. Interestingly, the main river of the region (the Po, which collects all regional river waters) was considerably more photoreactive than average, most likely due to inputs of agricultural nitrate from groundwater. This feature is positive from the point of view of photodegradation, because it ensures that all river waters (potentially carrying a pollution load) get effectively photoprocessed when eventually reaching the Po.

Paradoxically, contamination of surface waters by nitrate from agricultural activities would aid considerably in the photochemical degradation of pesticides, which also derive from agriculture. However, this “pollution fighting pollution” scenario has several limitations. First of all, nitrate yields  $\bullet\text{OH}$  and some of the studied pesticides react with  $\bullet\text{OH}$  to produce intermediates, which may be either more harmful (CTL, IPT) or about as harmful (ATZ) compared to the parent compound. Moreover, if pesticides occur in groundwater, the contamination of surface waters by aquifer discharge would occur also during winter, when photodegradation is slow. Still, leaching from groundwater coupled with photochemical degradation in river water (especially in spring-summer) is a potentially important dissipation route for the otherwise very persistent ATZ, which could account for its gradual disappearance from water environments.

Because of its fast degradation potential by direct photolysis and the production of intermediates with limited environmental impact, BTZ appears as the safest pesticide to be used among those under study, at least as far as photochemical depollution is concerned. Indeed, BTZ half-life times were never longer than 2.6 days (the upper limit refers to the highest-DOC sites), and were often

around half a day, especially in the Po river ( $t_{1/2} = 0.5$  days means  $l_{1/2} \sim 50$  km). Because the Po collects all the regional watercourses, effective BTZ photodecontamination would be ensured.

### ***Acknowledgements***

We are grateful to Dr. Elio Sesia (ARPA Piemonte) for providing us with the data of river-water chemistry. L.C. acknowledges Compagnia di San Paolo (Torino, Italy) for financially supporting his PhD fellowship.

### **References**

- Achleitner, S., De Toffol, S., Engelhard, C., Rauch, W., 2005. The European water framework directive: Water quality classification and implications to engineering planning. *Environ. Manag.* 35, 517-525.
- Al Housari, F., Höhener, P., Chiron, S., 2011. Factors responsible for rapid dissipation of acidic herbicides in the coastal lagoons of the Camargue (Rhône River Delta, France). *Sci. Total Environ.* 409, 582-587.
- ARPA (Agenzia Regionale per la Protezione Ambientale del Piemonte), 2020. <http://www.arpa.piemonte.it/approfondimenti/temi-ambientali/acqua/acque-superficiali-corsi-dacqua/documentazione-e-dati>, last accessed May 2020.
- Avetta, P., Marchetti, G., Minella, M., Pazzi, M., De Laurentiis, E., Maurino, V., Minero, C., Vione, D., 2014. Phototransformation pathways of the fungicide dimethomorph ((E, Z) 4-[3-(4-chlorophenyl)-3-(3, 4-dimethoxyphenyl)-1-oxo-2-propenyl] morpholine), relevant to sunlit surface waters. *Sci. Total Environ.* 500, 351-360.

- Barbosa, A. B., Domingues, R. B., Galvão, H. M., 2010. Environmental forcing of phytoplankton in a Mediterranean estuary (Guadiana Estuary, South-western Iberia): A decadal study of anthropogenic and climatic influences. *Estuar. Coasts* 33, 324-341.
- Bassanino, M., Sacco, D., Zavattaro, L., Grignani, C., 2011. Nutrient balance as a sustainability indicator of different agro-environments in Italy. *Ecol. Indic.* 11, 715–723.
- Bodrato, M., Vione, D., 2014. APEX ( Aqueous Photochemistry of Environmentally occurring Xenobiotics ): a free software tool to predict the kinetics of photochemical processes. *Environ. Sci. Process. Impacts* 16, 732–740.
- Braslavsky, S.E., 2007. Glossary of terms used in photochemistry. third edition. *Pure Appl. Chem.* 79, 293-465.
- Brezonik, P. L., Fulkerson-Brekken, J., 1998. Nitrate-induced photolysis in natural waters: Controls on concentrations of hydroxyl radical photo-intermediates by natural scavenging agents. *Environ. Sci. Technol.* 32, 3004-3010.
- Carena, L., Puscasu, C. G., Comis, S., Sarakha, M., Vione, D., 2019. Environmental photodegradation of emerging contaminants: A re-examination of the importance of triplet-sensitised processes, based on the use of 4-carboxybenzophenone as proxy for the chromophoric dissolved organic matter. *Chemosphere* 237, article n. 124476.
- Carena, L., Vione, D., 2020. Mapping the photochemistry of European mid-latitudes rivers: An assessment of their ability to photodegrade contaminants. *Molecules* 25, article n. 424.
- Carena, L., Fabbri, D., Passananti, M., Minella, M., Pazzi, M., Vione, D., 2020. The role of direct photolysis in the photodegradation of the herbicide bentazone in natural surface waters. *Chemosphere* 246, article n. 125705.
- Castiglioni, S., Bagnati, R., Fanelli, R., Pomati, F., Calamari, D., Zuccato, E. (2006) Removal of pharmaceuticals in sewage treatment plants in Italy. *Environmental Science and Technology* 40(1), 357-363.

- Chung, S. W., Gu, R. R., 2009. Prediction of the fate and transport processes of atrazine in a reservoir. *Environ. Manag.* 44, 46-61.
- Debernardi, L., De Luca, D.A., Lasagna, M., 2008. Correlation between nitrate concentration in groundwater and parameters affecting aquifer intrinsic vulnerability. *Environmental Geol.* 55, 539–558.
- Fabbri, D., Minella, M., Maurino, V., Minero, C., Vione, D., 2015. Photochemical transformation of phenylurea herbicides in surface waters: A model assessment of persistence, and implications for the possible generation of hazardous intermediates. *Chemosphere* 119, 601-607.
- Fenner, K., Canonica, S., Wackett, L. P., Elsner, M., 2013. Evaluating pesticide degradation in the environment: blind spots and emerging opportunities. *Science* 341, 752–758.
- Fono, L. J., Kolodziej, E. P., Sedlak, D. L., 2006. Attenuation of wastewater-derived contaminants in an effluent-dominated river. *Environ. Sci. Technol.* 40, 7257-7262.
- Franchino, E., Lasagna, M., Bucci, A., De Luca, D.A., 2014. Statistical analysis of groundwater nitrate concentrations in piedmont plain aquifers (north-western Italy), in: *Proceeding of Flowpath 2014—National Meeting on Hydrogeology, Viterbo (Italy)*, June 18–20. pp. 62–63.
- Galichet, F., Maillhot, G., Bonnemoy, F., Bohatier, J., Bolte, M., 2002. Iron(III) photo-induced degradation of isoproturon: correlation between degradation and toxicity. *Pest. Manag. Sci.* 58, 707-712.
- Gerecke, A.C., Canonica, S., Muller, S.R., Scharer, M., Schwarzenbach, R.P. (2001). Quantification of dissolved natural organic matter (DOM) mediated phototransformation of phenylurea herbicides in lakes. *Environ. Sci. Technol.* 35, 3915-3923.
- Godinho, F. N., Ferreira, M. T., Santos, J. M., 2000. Variation in fish community composition along an Iberian river basin from low to high discharge: relative contributions of environmental and temporal variables. *Ecol. Freshwat. Fish* 9, 22-29.

- Halladja, S., Amine-Khodja, A., ter Halle, A., Boulkamh, A., Richard, C., 2007. Photolysis of fluometuron in the presence of natural water constituents. *Chemosphere* 69, 1647-1654.
- Kilsby, C. G., Teller, S. S., Fowler, H. J., Howels, T. R., 2007. Hydrological impacts of climate change on the Tejo and Guadiana rivers. *Hydrol. Earth Syst. Sci.* 11, 1175-1189.
- Lasagna, M., De Luca, D.A., 2019. Evaluation of sources and fate of nitrates in the western Po plain groundwater ( Italy ) using nitrogen and boron isotopes. *Environ. Sci. Pollut. Res.* 26, 2089–2104.
- Lasagna, M., De Luca, D.A., Franchino, E., 2016a. Nitrate contamination of groundwater in the western Po Plain ( Italy ): the effects of groundwater and surface water interactions. *Environ. Earth Sci.* 75, 240.
- Lasagna, M., De Luca, D.A., Franchino, E., 2016b. The role of physical and biological processes in aquifers and their importance on groundwater vulnerability to nitrate pollution. *Environ. Earth Sci.* 75.
- Marchetti, G., Minella, M., Maurino, V., Minero, C., Vione, D., 2013. Photochemical transformation of atrazine and formation of photointermediates under conditions relevant to sunlit surface waters: Laboratory measures and modelling. *Wat. Res.* 47, 6211-6222.
- Martinelli, G., Dadomo, A., De Luca, D.A., Mazzola, M., Lasagna, M., Pennisi, M., Pilla, G., Sacchi, E., Saccon, P., 2018. Nitrate sources, accumulation and reduction in groundwater from Northern Italy: Insights provided by a nitrate and boron isotopic database. *Appl. Geochemistry* 91, 23–35.
- McConnell, L. L., Harman-Fetcho, J. A., Hagy, J. D., 2004. Measured concentrations of herbicides and model predictions of atrazine fate in the Patuxent river estuary. *J. Environ. Qual.* 33, 594-604.
- McNeill, K., Canonica, S., 2016. Triplet state dissolved organic matter in aquatic photochemistry: Reaction mechanisms, substrate scope, and photophysical properties. *Environ. Sci.: Processes Impacts* 18, 1381-1399.



- Minella, M., Leoni, B., Salmaso, N., Savoye, L., Sommaruga, R., Vione, D., 2016. Long-term trends of chemical and modelled photochemical parameters in four Alpine lakes. *Sci. Total Environ.* 541, 247-256.
- NCAR (National Center for Atmospheric Research), 2020. Quick TUV calculator [WWW Document]. URL [http://cprm.acom.ucar.edu/Models/TUV/Interactive\\_TUV/](http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/) (accessed March 2020).
- Ongley, E. D., Xiaolan, Z., Tao, Y., 2010. Current status of agricultural and rural non-point source pollution assessment in China. *Environ. Pollut.* 158, 1159-1168.
- Pace, A., Barreca, S., 2014. Environmental Organic Photochemistry: Advances and Perspectives. *Curr. Org. Chem.* 17, 3032-3041.
- Parizi, M. P. S., Acosta, A. M. L., Ishiki, H. M., Rossi, R. C., Mafra, R. C., Teixeira, A. C. S. C., 2019. Environmental photochemical fate and UVC degradation of sodium levothyroxine in aqueous medium. *Environ. Sci. Pollut. Res.* 26, 4393-4403.
- Poulain, L., Mailhot, G., Wong-Wah-Chung, P., Bolte, M., 2003. Photodegradation of chlortoluron sensitised by iron(III) aquacomplexes. *J. Photochem. Photobiol. A: Chem.* 159, 81-88.
- QGIS Developmental Team, 2020. QGIS Geographic Information System. Open Source Geospatial Foundation Project; 2018. Accessed April 2020.
- Remucal, C. K., 2014. The role of indirect photochemical degradation in the environmental fate of pesticides: a review. *Environ. Sci.: Processes Impacts* 16, 628-653.
- Richardson, S. D., Ternes, T. A., 2014. Water analysis: Emerging contaminants and current issues. *Anal. Chem.* 86, 2813-2848.
- Rosario-Ortiz, F. L., Canonica, S., 2016. Probe compounds to assess the photochemical activity of dissolved organic matter. *Environ. Sci. Technol.* 50, 12532-12547.
- Shankar, M.V., Nélieu, S., Kerhoas, L., Einhorn, J., 2008. Natural sunlight  $\text{NO}_3^-/\text{NO}_2^-$ -induced photo-degradation of phenylurea herbicides in water. *Chemosphere* 71, 1461-1468.

- Silva, E., Mendes, M. P., Ribeiro, L., Cerejeira, M. J., 2012. Exposure assessment of pesticides in a shallow groundwater of the Tagus vulnerable zone (Portugal): A multivariate statistical approach (JCA). *Environ. Sci. Pollut. Res.* 19, 2667-2680.
- Song, N.-H., Bu, Y.-J., Shan, Z.-J., 2010. A review of studies on pesticide pollution in surface water. *J. Ecol. Rural Environ.* 26, 49-57.
- Vione, D., Das, R., Rubertelli, F., Maurino, V., Minero, C., Barbati, S., Chiron, S., 2010. Modelling the occurrence and reactivity of hydroxyl radicals in surface waters: implications for the fate of selected pesticides. *Intern. J. Environ. Anal. Chem.* 90, 260-275.
- Vione, D., Minella, M., Maurino, V., Minero, C., 2014. Indirect photochemistry in sunlit surface waters: Photoinduced production of reactive transient species. *Chemistry Eur. J.* 20, 10590-10606.
- Vione, D., Encinas, A., Fabbri, D., Calza, P., 2018. A model assessment of the potential of river water to induce the photochemical attenuation of pharmaceuticals downstream of a wastewater treatment plant (Guadiana River, Badajoz, Spain). *Chemosphere* 2018, 473-481.
- Vione, D., Scozzaro, A., 2019. Photochemistry of surface fresh waters in the framework of climate change. *Environ. Sci. Technol.* 53, 7945-7963.
- Vione, D., 2020. A critical view of the application of the APEX software (Aqueous Photochemistry of Environmentally-occurring Xenobiotics) to predict photoreaction kinetics in surface freshwaters. *Molecules* 25, article n. 9.
- Zhou, C. Z., Chen, J. W., Xie, H. J., Zhang, Y. N., Li, Y. J., Wang, Y., Xie, Q., Zhang, S. Y., 2018. Modeling photodegradation kinetics of organic micropollutants in water bodies: A case of the Yellow River estuary. *J. Hazard. Mat.* 349, 60-67.