



Occurrence and spatial-temporal distribution of atrazine and its metabolites in the aquatic environment of the Volturno River estuary, southern Italy



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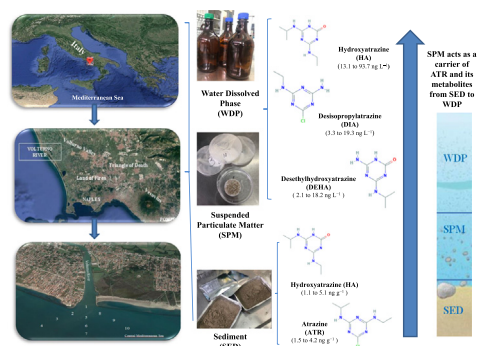
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HIGHLIGHTS

- The first study is about atrazine and its metabolites in South Italy.
- Despite being banned for many years, these pollutants are still present.
- The desethylatrazine-to-atrazine ratio was >0.5 indicating a long residence time.
- Atrazine and its metabolites levels were higher southward in the winter period.

GRAPHICAL ABSTRACT



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ABSTRACT

The present study assesses the spatial distribution and temporal trends of the water dissolved phase (WDP), suspended particulate matter (SPM) and sediment partitioning of atrazine (ATR) and its metabolites in the Volturno River estuary. The load contribution of ATR and its metabolites in this river to the Central Mediterranean Sea was estimated. Samples were collected in 10 sampling sites during the four seasons. The total concentrations of ATR and DPs detected ranged from 18.1 to 105.5 ng L⁻¹ in WDP, from 4.5 to 63.2 ng L⁻¹ in SPM, and from 4.6 to 18.6 ng g⁻¹ in sediment samples, indicating high levels of these pollutants. Structural equation model and the ratio study indicated that the relationship between sediment and WDP pollutants occurred through the SPM. The pollutants load at the Volturno River in its mouth was evaluated in about 30.4 kg year⁻¹, showing that this river is an important source of these analytes through discharge into Central Mediterranean Sea. Principal component analysis indicated that ATR and its metabolites pollution moves from Volturno River mouth southward and increased in the rainy season. The desethylatrazine-to-atrazine ratio was higher than 0.5 for all samples analyzed, indicating an historical discharge and a long residence time of ATR in sediment about two decades after its ban, and classifying ATR as a nonpoint source contaminant. This study makes up the first record of ATR and its metabolites in superficial water of Southern Italy and provides helpful data as starting point for future studies.

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1. Introduction

In the last few decades, many concerns have been raised about the use of pesticides in agriculture, associated mainly to the negative effects they can exert both on terrestrial and aquatic environments, as well as on human health (Corcoran et al., 2020; Cui et al., 2019; Ghirardelli et al., 2020).

The threat of pesticides is due to their persistence and chemical and physical characteristics and, above all, their ability to metabolize, giving place to new degradation products (DPs) (Climent et al., 2019; Della Flora et al., 2019; Ouyang et al., 2019; Qu et al., 2018; Sun et al., 2019). DPs are formed through chemical degradation (e.g. photolysis, oxidation and reduction reactions) or biological degradation through the action of microorganisms usually distributed in the first few centimetres of the soil (Cardeal et al., 2011). Usually, the formed DPs are at least as toxic as the parent compounds, and due highly polar and hydrophilic characteristics they can easily reach aquatic environments through leaching from the soil (Farlin et al., 2013; Sun et al., 2019). These metabolites represent a serious risk to human health; indeed, they could cause the onset of diseases affecting dermatological, gastrointestinal, neurological, immune, respiratory, reproductive and endocrine systems (De Geronimo et al., 2014; Montiel-León et al., 2019; Sun et al., 2019; Wang et al., 2019; Yu et al., 2018).

Atrazine (ATR) is among the most used pesticides with its high amount applied annually all over the world. The main ATR metabolites are desethylatrazine (DEA), desisopropylatrazine (DIA), hydroxyatrazine (HA), desethylhydroxyatrazine (DEHA) and desisopropylhydroxyatrazine (DIHA) (Fig. 1). ATR may be found in the soil-water environment because of its high mobility (Benvenuto et al., 2010; Montiel-León et al., 2019) and high environmental persistence with consequent pollution of both surface water and sediment (Battaglin et al., 2018; Gonsioroski et al., 2020). The half-life of ATR varies from several weeks to about two years in different environmental matrices (Gilliom et al., 2006), mainly because its non-biodegradable properties (Jiang et al., 2020; Liu et al., 2020; Singh et al., 2020) and their resistance to microbiological degradation in aquatic systems (Barchanska et al., 2017; Cruzeiro et al., 2016). ATR is classified in Group III as a possible carcinogenic to humans and it may cause adverse

effects on human health including acute and chronic toxicity, genotoxicity and reproductive toxicity. Moreover, it acts as an endocrine disruptor and it has been reported that exerts an estrogen-like activity in ovarian cancer cells (Yin et al., 2020).

The presence of ATR and its metabolites in water has been reported in countries where this herbicide is still used, as in Iran, USA, South Africa, China and Canada (Almasi et al., 2020; Ali et al., 2018; Farounbi and Ngqwala, 2020; Montiel-León et al., 2019) but also in countries where ATR has been banned for years (Barchanska et al., 2017; Benvenuto et al., 2010; Carafa et al., 2007). In Europe, ATR was finally banned in 2004 (Commission Decision 2004/248/EC, 2004) and it is still regularly detected in across surface water and sediment (Caquet et al., 2013; Masiá et al., 2015; Rodríguez-González et al., 2016). Moreover, it is still found in Canadian (Montiel-León et al., 2019) and French drinking water (Le Coadou et al., 2017). The European Directive (Directive, 2013/39/EU) establishes environmental Quality Standards of 0.6 µg/L as annual average and 2.0 µg/L as maximum allowable concentration of ATR for fresh waters.

Among the 20 European Union (EU) member states for which complete data are available, Italy is the third EU state for the sale of pesticides in 2016 with nearly 60 million kg sold each year (EUROSTAT, 2018). Indeed, recent studies reported the presence of ATR and its DPs in water of Italy (Ghirardelli et al., 2020; Hakoun et al., 2017; Lerch et al., 2018; Sassine et al., 2017; Vonberg et al., 2014a). In the Campania region, southern Italy, thanks to the high fertility of the territory due to the large presence of volcanic soils distributed throughout the region, agricultural activity is highly developed since ancient Roman times. In particular, Piana del Volturno represents an area of intensive agriculture crossed by the Volturno River, that receives high quantity of different contaminants from farms, chemical factory discharges, urban sewages and agricultural run-off (Isidori et al., 2004; Triassi et al., 2019).

The main aim of this study was to assess the concentrations of ATR and its metabolites in the Volturno River estuary, and their environmental impact on Central Mediterranean Sea. Particularly, the present study aims to i) assess their concentration levels; ii) estimate their inputs into the Central Mediterranean Sea; iii) evaluate their water and sediment partitioning; and iv) define the spatial distribution and temporal trends in the Volturno River estuary.

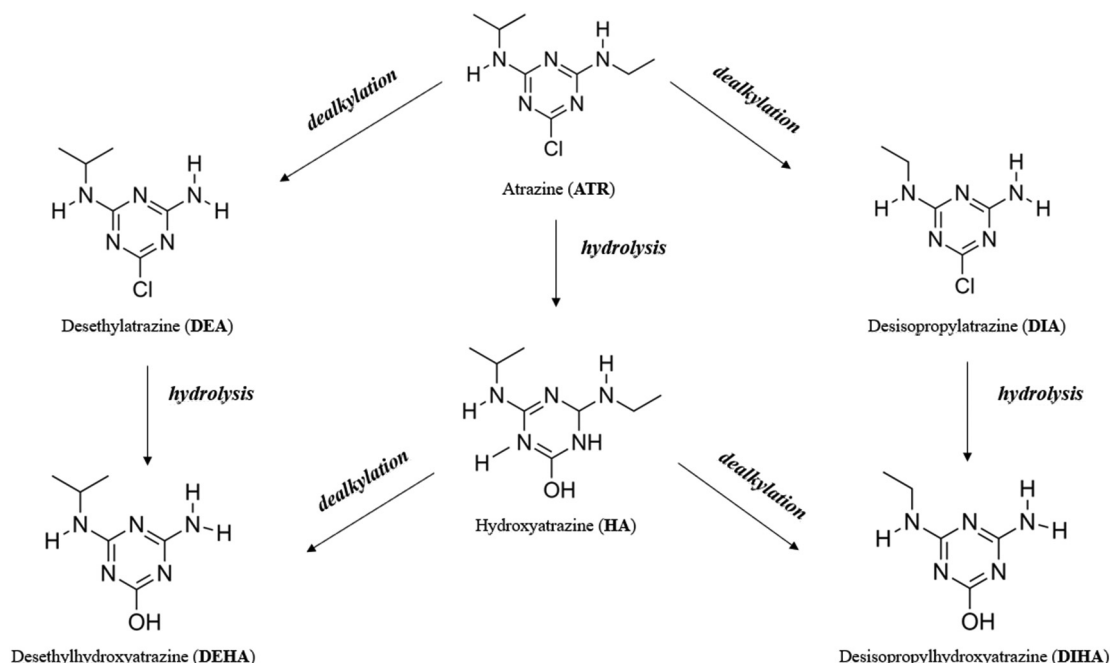


Fig. 1. Major metabolic pathways of atrazine (ATR).

2. Materials and methods

2.1. Study area

The Volturno River is one of the most important rivers in the South of Italy (Fig. 2), with a length of 175 Km and an annual flow of 82.1 m³/s. It crosses a huge area of Campania region, once called Campania Felix by the ancient Romans, indicating high productivity of the region, due to the fertile volcanic soils. The temperate and pleasant climate made this territory famous and renowned also for the woods and the extraordinary landscape with historical, cultural and agri-food traditions unique in the world. Today as in the past, an important agricultural activity has developed in this land which represents one of the main primary sectors of the Campania region. Several agricultural products are grown in these territories such as apples, tomatoes, lemons. The huge spread of agri-food sector in Campania lead to water quality deterioration because of the input of pesticides and fertilizers (Esposito et al., 2018), which are among the main factors of chemical and biological pollution (Verde et al., 2013).

2.2. Sampling

Between 2017 and 2018, water and sediment samples were collected to assess the presence of ATR and its metabolites. The sampling was carried out during four seasons, in November 2017 and February, April and July 2018. Regarding the sediments, the samples were taken only during the spring campaign, at 10 different sampling points. One sample was collected at the mouth of the river and in other nine sampling points at different distances (i.e., 500 m, 1000 m and 1500 m) at north, south and west estuary directions (Fig. 2), in order to have a proper idea of the evolution of the contamination downriver. In each site, surface water samples were taken with pre-cleaned 2.5 L glass bottles, transferred to the laboratory and stored at 4 °C until analysis. Water samples were filtered through a previously kiln-fired (400 °C overnight) GF/F glass fiber filter (47 mm × 0.7 µm; Whatman, Maidstone, UK): the

filtrate corresponds to the dissolved phase (WDP), while the solids retained on the filter represent the suspended particulate matter (SPM).

Filters were kept in the dark at -20 °C until analysis, while for filtrates, preserved in the dark at 4 °C, the analysis was performed about 3-6 h from sampling. Surface sediment (0-5 cm) samples were collected and placed in aluminium containers by a grab sampler (Van Veen Bodemhappe 2 L capacity), then they were transferred to the laboratory and stored at -20 °C before analysis.

2.3. Extraction of water and sediment samples

A multi-residue method proposed by Climent et al. (2018) was used for ATR determination. Briefly, water samples (500 mL) were filtrated with glass fiber filters (0.45 µm) and the filtrates were preconcentrated with a peristaltic pump at a constant flow of 7 mL min⁻¹ by SPE Oasis HLB cartridges, preconditioned with 5 mL of acetone, 5 mL of acetonitrile and 10 mL of Milli-Q water. After this loading step the cartridges were dried for 5 min under air stream, and elution with 4 mL of acetone and 4 mL of acetonitrile was performed. The samples were dried under nitrogen stream and redissolved in 500 µL of methanol/water (1:1) for analysis by LC-MS/MS.

The suspended particulate matter was gravimetrically determined, after drying the filter in an air-heated oven (55 °C until constant weight) and equilibrated at room temperature in a desiccator. Filters were extracted three times by sonication with 10 mL of methanol/acetone (1:1) for 15 min. The extracts were evaporated to dryness under a gentle nitrogen flow and reconstituted with 500 µL of methanol/water (1:1) for analysis by LC-MS/MS (Pose-Juan et al., 2014; Cruzeiro et al., 2016).

For sediment, 10 mL of methanol/acetone (1:1) were added to 5.0 g of sample for ultrasonic extraction, followed by centrifugation for 15 min at 3000 rpm (Pose-Juan et al., 2014). The supernatant was transferred into a glass vial and solvents were evaporated until dryness under nitrogen stream. The dried extract was redissolved in 500 µL of methanol/water (1:1) for its analysis by LC-MS/MS.



Fig. 2. Map of the study areas and sampling sites in the Volturno River estuary, southern Italy.

2.4. Analytical determination of atrazine and its degradation products

To evaluate ATR and its DPs concentrations, extracts were analyzed by LC-MS/MS. Analyses were performed using Thermo Scientific™ UltiMate™ 3000UHPLC coupled to TSQ Fortis Triple Quadrupole MS. Analytes separation was achieved by a reversed phase Acclaim C18 column (4 µm particle size, 250 × 4.6 mm). The mobile phase contains water/methanol (95:5) (LC-MS grade) as eluent A and methanol/water (95:5) (LC-MS grade) as eluent B, each with 0.1% formic acid/5 mM ammonium formate. The column temperature was set to +25 °C, the flow rate to 300 µL min⁻¹ and the injection volume was 2 µL. A gradient elution was performed by varying the proportion of solvent A to solvent B: 0 min 2.0% B, 1 min 2% B, 2 min 50% B, 9 min 98% B, 12 min 98% B and 12.1 min 2% B. Total analysis time per sample was 17 min. Ionization and fragmentation settings were optimized by direct injection of pesticide standard solutions. MS/MS was performed in the selected reaction monitoring mode (SRM) with electrospray ionization (ESI) in positive mode. For each compound, two characteristic product ions of the protonated molecule [M + H]⁺ were monitored, the first and most abundant one was used for quantification (SRM₁), while the second one was used as a qualifier (SRM₂). LC-MS/MS conditions are shown in detail in Tables S1 and S2.

2.5. Quality control and quality assurance

Method validation was performed in order to evaluate the data quality through the determination of precision, accuracy, linearity, limit of detection (LOD), limit of quantification (LOQ) and uncertainty. The same extraction procedures were applied to standards, blanks and samples to check for interfering substances, moreover for each batch of 10 samples analyzed, certified reference materials were run in the same way as samples. The surrogate standard used for the LC-MS/MS analysis was Terbutylazine (Dr. Ehrenstorfen). This standard was added to the samples before extraction to monitor the efficiency of the analytical procedure. The LODs and LOQs were estimated as 3 and 10 times the signal/noise ratio for each analyte; in particular, for WDP and SPM the LODs and LOQs ranges were 0.000375-0.000615 ng L⁻¹ and 0.00125-0.00205 ng L⁻¹, respectively. In sediment samples the values range were 0.000875-0.00121 ng g⁻¹ and 0.00292-0.00403 ng g⁻¹, respectively.

The surrogate averaged recoveries were 92.5 ± 7.2% in the WDP, 90.1 ± 6.8% in the SPM, and 91.1 ± 4.0% in the sediment samples. Resulting data for ATR and DPs were corrected for surrogate recoveries.

2.6. Statistical analysis and calculation of the pollutant inputs

The statistical software SPSS, version 22 for Windows (SPSS Inc., Chicago, IL, USA) was used to perform results analysis, expressed as the pesticide average concentration ± standard deviation (SD). A *p* value ≤ 0.05 was considered statistically significant. The annual pollutant load was evaluated according to the UNEP guidelines (UNEP and MAP, 2004), widely approved (HELCOM, 1993; Steen et al., 2001). A flow-averaged mean amount was obtained as the product of instantaneous concentration and the daily averaged water flow discharge for each sampling event and corrected by the total water load for the sampling period (November 2017 – July 2018) (Montuori and Triassi, 2012). River flow data were found in database of the Autorità di Bacino Nazionale dei Fiumi Liri-Garigliano e Volturno (Piano di gestione acque, ciclo 2015-2021, 2018).

Structural Equation Model (SEM) has become a useful research technique to analyze the relationships between latent variables. The covariance-based SEM (Jöreskog, 1970) and the variance-based method (Wold, 1975) are two approaches to estimating the relationships in a SEM. In this paper, it was chosen the partial least squares (PLS) approach, performed by Smart-PLS (Version 3), because it has less

stringent assumptions for the distribution of variables and error terms (Wold, 1975).

Principal component analysis (PCA) is a multivariate technique for examining relationships among several quantitative variables (Pearson, 1901 and Hotelling, 1933). The PCA decreases the dimensionality of a set of data and provides to preserve the structure. The first principal component is the linear combination of the original variables that accounts for the greatest possible variance. Each subsequent principal component is the linear combination of the original variables that has the greatest possible variance and is uncorrelated with the previously defined components. In the PCA there are three main criteria to select the components to retain: Eigenvalue one criterion (the first components with Eigenvalues higher than 1 will be chosen); Amount of explained variance (the chosen factors should explain 70 to 80% of your variance at least); Scree plot.

3. Results and discussion

3.1. Occurrence of atrazine and its degradation products

ATR and its DPs were detected in all water and sediment samples and the data obtained were shown in Tables 1a, 1b and 2. The concentrations of ATR and DPs found in WDP (Table 1a), ranged from 0.13 to 8.22 ng L⁻¹ with a mean value of 3.42 ng L⁻¹ for ATR, from 1.26 to 9.35 ng L⁻¹ with a mean value of 5.01 ng L⁻¹ for DIHA, from 1.12 to 13.18 ng L⁻¹ with a mean value of 6.46 ng L⁻¹ for DEHA, from 2.31 to 10.79 ng L⁻¹ with a mean value of 6.63 ng L⁻¹ for DIA, from 0.77 to 6.34 ng L⁻¹ with a mean value of 2.37 ng L⁻¹ for DEA and from 12.07 to 59.32 ng L⁻¹ with a mean value of 30.48 ng L⁻¹ for HA. The concentrations of ATR and DPs found in SPM (Table 1b), ranged from 0.57 to 44.28 ng g⁻¹ with a mean value of 14.93 ng g⁻¹ for ATR, from 0.44 to 59.40 ng g⁻¹ with a mean value of 22.24 ng g⁻¹ for DIHA, from 5.49 to 74.92 ng g⁻¹ with a mean value of 28.52 ng g⁻¹ for DEHA, from 5.05 to 83.21 ng g⁻¹ with a mean value of 33.48 ng g⁻¹ for DIA, from 0.29 to 21.14 ng g⁻¹ with a mean value of 6.48 ng g⁻¹ for DEA and from 11.10 to 332.17 ng g⁻¹ with a mean value of 132.06 ng g⁻¹ for HA.

A review of the literature (Table 3) suggests that ATR and some of its DPs (mainly DEA and DIA) are widespread in waters around the world. Compared to aquatic environments from Europe (Table 3), the levels found in WDP in our study were higher than those found in rivers such as Danube River in Hungary (Takáts et al., 2001) and Serbia (Radovic et al., 2015), in Ebro Delta (Benvenuto et al., 2010) and Llobregat River (Masiá et al., 2015) from Spain, in Brittany River, France (Gervais et al., 2008); and Italian rivers such as the Arno River (Bono and Magi, 2013), and likewise in the Baltic Sea (Germany) and Northern Aegean Sea (Italy) (Nödler et al., 2013). On contrary, the concentrations of ATR and its DPs were lower than those reported in Klodnica River (Poland) (Barchanska et al., 2017), in Billiers River (Caquet et al., 2013) and Vannetin River from France (Irace-Guigand et al., 2004), in Spanish Duero River, Miño River and Ebro River (Hildebrandt et al., 2008; Gómez-Gutiérrez et al., 2006; Claver et al., 2006; Navarro et al., 2010), in Scheldt River in Netherlands (Steen et al., 2001) and Belgium (Noppe et al., 2007), in Tagus River (Portugal) (Cruzeiro et al., 2016; Silva et al., 2015), as well as in Italian Po River (Ghirardelli et al., 2020). Finally, similar levels were found in Sacca di Goro (Italy) by Carafa et al. (2007) and in Ebro River (Spain) by Benvenuto et al. (2010), except for DEA and HA, whose concentrations were higher than those found in Volturno River.

The total concentrations of ATR and DPs in WDP ranged from 18.1 to 105.5 ng L⁻¹ with mean value of 54.4 ng L⁻¹ and from 4.5 to 63.2 ng L⁻¹ with mean value of 28.4 ng L⁻¹ (237.7 ng g⁻¹) in SPM. The data obtained showed that the highest concentrations were found in WDP. Currently, there are few studies that have evaluated the presence of ATR and its DPs both in WDP and SPM samples, making it difficult to compare the results of this study with those in the literature. In particular, Darwano et al. (2014) and Cruzeiro et al. (2016) reported DEA levels in SPM of

Table 1aDescription of the sampling sites and mean concentrations (\pm standard deviations) of ATR and its metabolites in the water dissolved phase (WDP) of the Volturno River, southern Italy.

Sampling location				Compound in WDP ng L ⁻¹						
Site number identification	Site characteristics	Site location	Campaigns	ATR	DIHA	DEHA	DIA	DEA	HA	Sum ATR and its DPs
1 (river water)	Volturno River mouth	41°01'19"N 13°55'26"E	November	6.70 \pm 0.12	7.53 \pm 0.13	8.91 \pm 0.14	9.75 \pm 0.10	4.16 \pm 0.13	37.48 \pm 0.52	74.53 \pm 0.56
			February	8.22 \pm 0.17	9.35 \pm 0.14	13.18 \pm 0.14	10.79 \pm 0.44	6.34 \pm 0.07	57.68 \pm 0.82	105.55 \pm 1.08
			April	4.47 \pm 0.13	5.43 \pm 0.24	9.34 \pm 0.08	8.43 \pm 0.10	4.62 \pm 0.12	38.69 \pm 0.35	70.98 \pm 0.33
2 (sea water)	River mouth 500 m north	41°01'05"N 13°55'38"E	November	3.65 \pm 0.09	5.46 \pm 0.09	6.76 \pm 0.37	6.88 \pm 0.11	1.07 \pm 0.27	27.44 \pm 0.77	51.28 \pm 0.52
			February	4.96 \pm 0.13	8.23 \pm 0.14	8.14 \pm 0.17	7.36 \pm 0.31	3.11 \pm 0.20	46.88 \pm 0.21	78.69 \pm 0.38
			April	3.60 \pm 0.12	3.44 \pm 0.63	5.02 \pm 0.52	4.59 \pm 0.12	2.47 \pm 0.52	22.65 \pm 0.10	41.79 \pm 1.76
3 (sea water)	River mouth 1000 m north	41°00'51"N 13°55'48"E	November	1.35 \pm 0.09	5.26 \pm 0.42	4.23 \pm 0.49	7.61 \pm 0.14	1.17 \pm 0.30	21.67 \pm 0.14	41.32 \pm 1.11
			February	3.59 \pm 0.29	6.85 \pm 0.15	8.06 \pm 0.13	6.84 \pm 0.21	2.82 \pm 0.22	44.55 \pm 0.37	72.73 \pm 0.27
			April	1.21 \pm 0.08	2.55 \pm 0.10	4.07 \pm 0.21	4.10 \pm 0.25	1.01 \pm 0.21	19.98 \pm 0.41	32.95 \pm 0.68
4 (sea water)	River mouth 1500 m north	41°00'33"N 13°55'49"E	November	1.67 \pm 0.14	3.04 \pm 0.24	3.42 \pm 0.48	6.82 \pm 0.48	0.93 \pm 0.19	20.46 \pm 0.09	36.36 \pm 0.77
			February	3.21 \pm 0.07	5.87 \pm 0.20	7.47 \pm 0.26	6.36 \pm 0.18	3.31 \pm 0.13	42.12 \pm 0.01	68.35 \pm 0.52
			April	1.16 \pm 0.10	2.46 \pm 0.60	2.48 \pm 0.12	4.26 \pm 0.09	0.83 \pm 0.54	16.14 \pm 0.29	27.37 \pm 1.21
5 (sea water)	River mouth 500 m west	41°01'25"N 13°55'56"E	November	4.25 \pm 0.09	9.04 \pm 0.18	9.57 \pm 0.13	8.93 \pm 0.35	3.70 \pm 0.19	26.27 \pm 0.15	61.78 \pm 0.48
			February	5.73 \pm 0.10	5.81 \pm 0.09	6.74 \pm 0.09	8.85 \pm 0.85	1.69 \pm 0.02	59.32 \pm 0.37	88.15 \pm 1.17
			April	3.64 \pm 0.12	3.33 \pm 0.09	5.61 \pm 0.09	5.21 \pm 0.09	1.62 \pm 0.45	30.88 \pm 0.12	50.30 \pm 0.71
6 (sea water)	River mouth 1000 m west	41°01'00"N 13°54'52"E	November	3.28 \pm 0.10	3.73 \pm 0.44	5.05 \pm 0.25	6.19 \pm 0.22	2.04 \pm 0.10	18.45 \pm 0.24	38.76 \pm 0.56
			February	3.92 \pm 0.17	5.37 \pm 0.25	6.34 \pm 0.08	8.48 \pm 0.09	1.42 \pm 0.37	26.31 \pm 0.24	51.86 \pm 0.63
			April	4.92 \pm 0.08	8.12 \pm 0.26	9.87 \pm 0.14	6.34 \pm 0.18	1.16 \pm 0.19	49.93 \pm 0.62	80.38 \pm 0.49
7 (sea water)	River mouth 1500 m west	41°00'45"N 13°54'40"E	November	2.93 \pm 0.09	3.55 \pm 0.13	5.07 \pm 0.21	4.01 \pm 0.19	1.42 \pm 0.10	29.50 \pm 0.13	46.50 \pm 0.33
			February	2.25 \pm 0.09	3.28 \pm 0.13	4.06 \pm 0.19	5.17 \pm 0.26	0.77 \pm 0.30	14.67 \pm 0.85	30.22 \pm 0.90
			April	3.76 \pm 0.12	5.16 \pm 0.13	4.50 \pm 0.75	7.91 \pm 0.59	1.06 \pm 0.20	19.25 \pm 0.07	41.67 \pm 1.40
8 (sea water)	River mouth 500 m south	41°01'30"N 13°55'10"E	November	4.47 \pm 0.11	7.04 \pm 0.11	10.51 \pm 0.10	5.55 \pm 0.63	2.54 \pm 0.18	46.90 \pm 0.75	77.02 \pm 0.99
			February	2.23 \pm 0.10	2.61 \pm 0.11	4.60 \pm 0.12	3.93 \pm 0.13	1.06 \pm 0.39	26.65 \pm 0.71	41.10 \pm 0.64
			April	1.68 \pm 0.13	2.15 \pm 0.26	3.14 \pm 0.18	5.20 \pm 0.50	1.54 \pm 0.18	12.25 \pm 0.10	25.98 \pm 1.02
9 (sea water)	River mouth 1000 m south	41°01'47"N 13°55'05"E	November	5.62 \pm 0.15	6.07 \pm 0.26	8.08 \pm 0.48	9.29 \pm 0.10	3.93 \pm 0.33	34.56 \pm 0.31	67.59 \pm 0.87
			February	6.58 \pm 0.11	8.86 \pm 0.09	11.33 \pm 0.11	9.32 \pm 0.43	5.49 \pm 0.11	54.50 \pm 0.11	96.09 \pm 0.93
			April	4.08 \pm 0.22	4.19 \pm 0.10	5.94 \pm 0.10	5.99 \pm 0.22	2.98 \pm 0.23	33.55 \pm 0.26	56.75 \pm 0.49
10 (sea water)	River mouth 1500 m south	41°02'02"N 13°54'56"E	November	3.39 \pm 0.23	4.21 \pm 0.21	6.38 \pm 0.49	6.74 \pm 0.41	4.49 \pm 0.26	20.96 \pm 0.36	46.20 \pm 1.51
			February	3.89 \pm 0.26	6.10 \pm 0.46	7.66 \pm 0.47	8.03 \pm 0.19	1.7 \pm 0.20	27.48 \pm 0.17	54.93 \pm 0.94
			April	4.25 \pm 0.10	7.78 \pm 0.12	10.84 \pm 0.43	8.49 \pm 0.12	3.86 \pm 0.19	51.72 \pm 0.28	86.97 \pm 0.30
10 (sea water)	River mouth 1500 m south	41°02'02"N 13°54'56"E	November	3.21 \pm 0.14	3.99 \pm 0.20	5.28 \pm 0.15	4.96 \pm 0.26	1.19 \pm 0.14	31.02 \pm 0.22	49.67 \pm 0.50
			February	2.16 \pm 0.36	4.01 \pm 0.07	4.16 \pm 0.28	6.36 \pm 0.13	4.15 \pm 0.21	18.63 \pm 0.30	39.52 \pm 0.73
			April	2.24 \pm 0.23	5.31 \pm 0.26	7.00 \pm 0.36	8.76 \pm 0.10	1.09 \pm 0.25	24.94 \pm 0.45	49.37 \pm 1.38
10 (sea water)	River mouth 1500 m south	41°02'02"N 13°54'56"E	November	3.86 \pm 0.14	7.36 \pm 0.09	10.45 \pm 0.66	8.16 \pm 0.11	2.49 \pm 0.02	48.22 \pm 0.22	80.57 \pm 0.57
			February	2.52 \pm 0.11	3.15 \pm 0.24	4.85 \pm 0.10	4.20 \pm 0.22	1.34 \pm 0.20	29.02 \pm 0.23	45.10 \pm 0.52
			April	1.86 \pm 0.10	3.14 \pm 0.13	3.91 \pm 0.26	5.04 \pm 0.33	2.91 \pm 0.15	16.98 \pm 0.86	33.86 \pm 0.49

ATR: atrazine; DIHA: desisopropylhydroxyatrazine; DEHA: desethylhydroxyatrazine; DIA: desisopropylatrazine; DEA: desethylatrazine; HA: hydroxyatrazine.

9 $\mu\text{g}/\text{kg}$ (mean value) in the Des Prairies River (Canada) and above 300 $\mu\text{g}/\text{kg}$ in the Tagus River estuary (Portugal), respectively. However, Climent et al. (2019) studied some of the most used pesticides in both WDP and SPM in Cachapoal River basin (Central Chile). The most frequently DPs found with the highest concentrations in the SPM were DIHA and HA (maximum 1123 $\mu\text{g}/\text{kg}$ and 1195 $\mu\text{g}/\text{kg}$, respectively). Comparing these data with the values of our study, the high concentrations found in SPM could be justified by the continuous application of ATR, which is still widely used for agriculture in Chile (Climent et al., 2019).

The higher concentrations in WDP were probably due to chlorotriazines (ATR, DIA, DEA) that are relatively polar compounds ($\log K_{ow}$ values between 1 and 3) (Barchanska et al., 2017; Noppe et al., 2007), while the presence of hydroxyatrazines (HA, DIHA, DEHA) is presumably due to hydrolysis occurring in water (Takáts et al., 2001). The main products in water via biotic mechanisms are DEA and DIA, but the highest concentrations are related to HA, DIHA and DEHA, because in water ATR is subjected to degradation processes such as hydrolysis, leading to dealkylation of the amino-groups, dechlorination and subsequent hydroxylation (Benvenuto et al., 2010), and also because mainly hydroxylated triazines are retained and accumulated both in water and sediment (Carafa et al., 2007). The presence of ATR in water samples could be due to its moderate solubility in water (33 mg/L at 20 °C) (Toledo-Jaldin et al., 2018) and because it is not

strongly adsorbed to sediment particles (Singh et al., 2018; Toledo-Jaldin et al., 2018).

In sediment, adsorption is the main process that controls the degradation and the mobility of an herbicide. Microbial degradation of ATR, which occurs by microorganisms, results in N-dealkylation to form primarily DEA and DIA. DEA is formed in higher concentrations than DIA probably because of 2–3 times faster removal of the ethyl group from DEA than the isopropyl group of DIA (Vonberg et al., 2014b). Moreover, DEA is less adsorbed, as well as DIA, onto sediment probably due to their less strongly sorption and higher mobility than ATR (Climent et al., 2019; Vonberg et al., 2014b).

The results showed mean concentrations of total ATR and DPs (Table 2) in the order following: HA (3.33 ng g⁻¹) > ATR (3.26 ng g⁻¹) > DEA (1.93 ng g⁻¹) > DEHA (1.75 ng g⁻¹) > DIA (0.81 ng g⁻¹) > DIHA (0.62 ng g⁻¹).

Compared with other studies, the concentrations of ATR and its DPs in the sediment samples from the Volturno River and estuary were higher than those found in Sacca di Goro by Carafa et al. (2007) and lower than those found for ATR in Danube River, Sava River and Morava River (Serbia) (Radovic et al., 2015), and for DIA in Guadalquivir River and Llobregat River (Spain) (Köck-Schulmeyer et al., 2013).

ATR and its metabolites concentrations in both water and sediment are shown in Fig. 3a and b. The ratios of total concentrations found in WDP and SPM ([WDP]/[SPM]), as well as those of the total

Table 1b
Description of the sampling sites and mean concentrations (\pm standard deviations) of ATR and its metabolites in the suspended particulate matter (SPM) of the Volturno River, southern Italy.

Sampling location			Compound in SPM ng L ⁻¹ (ng g ⁻¹)										Sum
Site number identification	Site characteristics	Site location	Campaigns	ATR	DIHA	DEHA	DIA	DEA	HA	Sum	ATR and its DPs		
1 (river water)	Volturno River mouth	41°01'19"N 13°55'26"E	November	3.58 ± 0.24	1.79 ± 0.20	6.34 ± 0.26	4.35 ± 0.21	1.20 ± 0.24	28.26 ± 0.24	45.68 ± 0.27	45.68 ± 0.27		
			February	5.02 ± 0.17	6.12 ± 0.19	49.62 ± 2.00	34.05 ± 1.64	9.43 ± 1.85	221.27 ± 1.88	356.43 ± 3.69	356.43 ± 3.69		
			April	44.28 ± 1.53	53.98 ± 1.65	45.10 ± 2.50	76.06 ± 3.74	21.14 ± 1.53	317.22 ± 1.94	557.80 ± 5.61	557.80 ± 5.61		
			July	18.40 ± 1.22	18.68 ± 1.64	27.34 ± 1.54	24.97 ± 0.90	6.85 ± 1.75	72.41 ± 1.15	168.65 ± 8.07	168.65 ± 8.07		
			November	43.81 ± 2.25	42.99 ± 2.13	74.92 ± 2.28	55.91 ± 2.25	14.36 ± 1.39	91.07 ± 3.69	323.06 ± 2.37	323.06 ± 2.37		
			February	1.40 ± 0.11	3.31 ± 0.11	1.98 ± 0.04	6.35 ± 0.16	0.32 ± 0.03	26.59 ± 0.27	39.97 ± 0.66	39.97 ± 0.66		
			April	1.15 ± 0.14	2.87 ± 0.22	3.49 ± 0.33	3.60 ± 0.36	0.43 ± 0.15	10.98 ± 0.28	22.52 ± 1.17	22.52 ± 1.17		
2 (sea water)	River mouth 500 m north	41°01'05"N 13°55'38"E	November	1.59 ± 0.19	0.33 ± 0.05	3.78 ± 0.26	1.88 ± 0.21	1.05 ± 0.09	22.78 ± 0.25	31.64 ± 0.43	31.64 ± 0.43		
			February	13.36 ± 1.64	2.76 ± 0.46	31.78 ± 2.20	15.86 ± 1.78	8.84 ± 0.75	191.72 ± 2.11	264.31 ± 6.37	264.31 ± 6.37		
			April	9.86 ± 1.23	24.52 ± 1.84	29.79 ± 2.83	30.71 ± 3.04	3.65 ± 1.30	93.75 ± 2.42	439.25 ± 7.31	439.25 ± 7.31		
			July	2.03 ± 0.11	1.25 ± 0.19	3.72 ± 0.20	2.12 ± 0.23	0.53 ± 0.12	4.44 ± 0.28	14.10 ± 0.09	14.10 ± 0.09		
			November	21.97 ± 1.15	13.52 ± 2.09	40.14 ± 2.18	22.95 ± 2.44	5.77 ± 1.28	47.92 ± 2.99	152.27 ± 0.96	152.27 ± 0.96		
			February	7.47 ± 0.92	0.95 ± 0.17	23.95 ± 1.94	11.21 ± 1.96	3.78 ± 0.94	137.44 ± 2.01	184.79 ± 4.24	184.79 ± 4.24		
			April	0.23 ± 0.02	2.95 ± 0.06	1.84 ± 0.11	5.84 ± 0.11	0.16 ± 0.02	22.38 ± 0.16	33.42 ± 0.17	33.42 ± 0.17		
3 (sea water)	River mouth 1000 m north	41°00'51"N 13°55'48"E	February	1.78 ± 0.16	22.37 ± 0.45	13.96 ± 0.39	44.25 ± 0.86	1.23 ± 0.13	169.43 ± 1.27	253.01 ± 1.26	253.01 ± 1.26		
			April	0.71 ± 0.16	2.04 ± 0.08	2.41 ± 0.38	3.10 ± 0.24	0.31 ± 0.12	8.02 ± 0.17	16.60 ± 0.33	16.60 ± 0.33		
			July	7.03 ± 1.60	20.15 ± 0.82	23.85 ± 3.79	30.66 ± 2.40	3.09 ± 1.23	79.27 ± 1.70	164.05 ± 3.25	164.05 ± 3.25		
			November	1.03 ± 0.08	0.57 ± 0.16	2.11 ± 0.15	2.03 ± 0.13	0.09 ± 0.01	2.58 ± 0.33	8.40 ± 0.75	8.40 ± 0.75		
			February	13.81 ± 1.04	7.61 ± 2.12	28.42 ± 1.96	27.22 ± 1.75	1.15 ± 0.14	34.69 ± 4.48	112.90 ± 1.98	112.90 ± 1.98		
			April	0.85 ± 0.14	0.07 ± 0.01	2.90 ± 0.21	0.84 ± 0.15	0.40 ± 0.12	16.50 ± 0.26	21.68 ± 0.20	21.68 ± 0.20		
			July	5.10 ± 0.83	0.44 ± 0.08	17.34 ± 1.26	5.36 ± 0.17	0.10 ± 0.02	98.69 ± 1.57	129.00 ± 1.98	129.00 ± 1.98		
4 (sea water)	River mouth 1500 m north	41°00'33"N 13°55'49"E	February	0.16 ± 0.01	2.53 ± 0.33	1.57 ± 0.14	5.36 ± 0.17	0.10 ± 0.02	20.87 ± 0.23	30.59 ± 0.61	30.59 ± 0.61		
			April	0.61 ± 0.16	1.58 ± 0.29	1.62 ± 0.29	2.39 ± 0.28	0.29 ± 0.07	72.68 ± 0.80	106.58 ± 2.12	106.58 ± 2.12		
			July	5.42 ± 1.43	14.11 ± 2.56	14.49 ± 2.63	21.42 ± 2.52	2.62 ± 0.65	61.90 ± 2.21	119.96 ± 10.67	119.96 ± 10.67		
			November	10.57 ± 1.25	2.72 ± 0.75	10.53 ± 0.78	10.12 ± 1.09	0.29 ± 0.04	11.10 ± 1.50	45.5 ± 0.50	45.5 ± 0.50		
			February	2.61 ± 0.23	1.83 ± 0.16	4.89 ± 0.26	2.85 ± 0.18	1.09 ± 0.14	25.44 ± 0.37	39.10 ± 0.67	39.10 ± 0.67		
			April	20.38 ± 1.81	14.30 ± 1.21	38.12 ± 1.99	22.24 ± 1.43	8.50 ± 1.07	198.25 ± 2.87	301.79 ± 8.21	301.79 ± 8.21		
			July	1.64 ± 0.10	5.48 ± 0.18	2.79 ± 0.22	7.93 ± 0.20	1.45 ± 0.12	30.72 ± 0.24	50.04 ± 0.42	50.04 ± 0.42		
5 (sea water)	River mouth 500 m west	41°01'25"N 13°55'56"E	February	12.56 ± 0.79	41.8 ± 1.35	21.25 ± 1.68	60.48 ± 1.52	11.09 ± 0.93	234.18 ± 1.82	381.37 ± 3.23	381.37 ± 3.23		
			April	2.36 ± 0.35	2.84 ± 0.26	3.71 ± 0.26	4.27 ± 0.27	0.83 ± 0.17	11.81 ± 0.22	25.82 ± 0.73	25.82 ± 0.73		

6 (sea water)	River mouth 1000 m west	41°01'00"N 13°54'52"E	July	(16.88 ± 2.72)	(21.33 ± 2.01)	(28.26 ± 1.98)	(31.99 ± 2.12)	(6.57 ± 1.28)	(90.51 ± 1.67)	(195.55 ± 5.62)
			November	(15.94 ± 1.29)	(17.82 ± 2.18)	(25.99 ± 1.40)	(21.36 ± 1.36)	(4.40 ± 0.87)	(35.52 ± 1.01)	(121.01 ± 5.44)
			February	(13.85 ± 1.35)	(14.71 ± 1.27)	(25.81 ± 2.10)	(19.10 ± 1.71)	(10.10 ± 1.13)	(173.69 ± 2.01)	(257.27 ± 3.44)
			April	(11.25 ± 1.55)	(38.11 ± 1.59)	(18.97 ± 1.69)	(57.05 ± 2.71)	(10.73 ± 2.29)	(224.28 ± 1.48)	(360.40 ± 5.33)
			July	(13.51 ± 1.66)	(17.68 ± 1.91)	(15.65 ± 0.60)	(27.50 ± 2.37)	(4.46 ± 0.82)	(68.70 ± 1.70)	(147.50 ± 5.98)
			November	(12.31 ± 2.14)	(9.83 ± 1.26)	(23.55 ± 1.10)	(15.39 ± 1.36)	(3.46 ± 0.51)	(35.44 ± 2.49)	(99.97 ± 6.23)
			February	(5.87 ± 1.26)	(18.57 ± 0.85)	(29.51 ± 1.47)	(17.44 ± 1.54)	(9.13 ± 1.15)	(113.54 ± 2.10)	(194.06 ± 1.38)
			April	(9.72 ± 1.20)	(30.77 ± 1.24)	(13.94 ± 1.09)	(51.22 ± 2.06)	(9.16 ± 1.28)	(135.14 ± 2.40)	(249.96 ± 6.67)
			July	(8.65 ± 1.20)	(15.02 ± 1.16)	(15.30 ± 1.41)	(3.46 ± 0.41)	(0.45 ± 0.05)	(8.08 ± 0.28)	(16.40 ± 0.53)
			November	(10.16 ± 1.17)	(11.26 ± 1.64)	(28.32 ± 2.71)	(11.96 ± 1.53)	(3.80 ± 0.90)	(24.97 ± 2.94)	(90.46 ± 5.27)
			February	(2.95 ± 0.20)	(20.81 ± 1.81)	(52.77 ± 1.71)	(29.81 ± 2.65)	(17.95 ± 1.71)	(250.69 ± 2.78)	(399.81 ± 4.43)
			7 (sea water)	River mouth 1500 m west	41°00'45"N 13°54'40"E	July	(13.91 ± 0.63)	(14.12 ± 0.73)	(35.76 ± 1.02)	(14.53 ± 1.72)
November	(28.07 ± 1.94)	(59.39 ± 1.99)				(28.75 ± 1.98)	(79.00 ± 3.06)	(6.52 ± 1.58)	(332.17 ± 1.84)	(533.91 ± 7.84)
February	(13.59 ± 1.66)	(29.81 ± 1.95)				(42.36 ± 3.05)	(45.79 ± 2.03)	(9.15 ± 1.51)	(124.38 ± 3.67)	(265.08 ± 9.51)
April	(29.69 ± 1.42)	(26.51 ± 2.68)				(45.97 ± 3.03)	(36.69 ± 2.46)	(8.14 ± 1.26)	(57.28 ± 3.25)	(204.28 ± 11.17)
July	(2.04 ± 0.09)	(2.07 ± 0.11)				(5.25 ± 0.15)	(2.13 ± 0.25)	(1.04 ± 0.10)	(26.37 ± 0.27)	(38.87 ± 0.08)
November	(13.91 ± 0.63)	(14.12 ± 0.73)				(35.76 ± 1.02)	(14.53 ± 1.72)	(7.11 ± 0.66)	(179.49 ± 1.84)	(264.92 ± 0.89)
February	(2.61 ± 0.23)	(5.94 ± 0.16)				(2.44 ± 0.25)	(7.50 ± 0.31)	(0.56 ± 0.10)	(30.56 ± 0.30)	(49.62 ± 1.17)
April	(1.46 ± 0.26)	(53.34 ± 1.45)				(21.94 ± 2.28)	(67.29 ± 2.80)	(5.03 ± 0.91)	(274.35 ± 2.69)	(445.41 ± 10.53)
July	(1.73 ± 0.18)	(27.09 ± 2.20)				(34.1 ± 0.34)	(3.70 ± 0.27)	(0.70 ± 0.06)	(10.54 ± 0.29)	(23.04 ± 1.41)
November	(19.88 ± 2.02)	(30.41 ± 2.87)				(46.88 ± 1.63)	(38.95 ± 3.70)	(6.47 ± 1.81)	(58.63 ± 2.30)	(201.22 ± 4.54)
February	(9.03 ± 1.19)	(11.54 ± 0.73)				(27.53 ± 1.28)	(17.03 ± 1.57)	(7.28 ± 1.15)	(165.56 ± 1.63)	(237.97 ± 4.47)
8 (sea water)	River mouth 500 m south	41°01'30"N 13°55'10"E				July	(3.78 ± 0.97)	(53.49 ± 2.89)	(18.49 ± 2.96)	(83.21 ± 3.94)
			November	(9.22 ± 1.39)	(16.01 ± 1.04)	(23.14 ± 1.49)	(24.95 ± 1.21)	(4.25 ± 0.72)	(77.37 ± 1.90)	(154.95 ± 0.53)
			February	(0.33 ± 0.08)	(4.61 ± 0.25)	(1.59 ± 0.26)	(7.16 ± 0.34)	(0.47 ± 0.11)	(21.74 ± 0.31)	(35.90 ± 0.93)
			April	(1.18 ± 0.18)	(2.06 ± 0.13)	(2.97 ± 0.19)	(3.20 ± 0.16)	(0.55 ± 0.09)	(9.93 ± 0.24)	(19.90 ± 0.07)
			July	(1.10 ± 0.11)	(1.51 ± 0.29)	(3.27 ± 0.20)	(1.84 ± 0.17)	(0.31 ± 0.10)	(4.12 ± 0.23)	(12.24 ± 0.16)
			November	(8.54 ± 0.88)	(11.80 ± 2.29)	(25.52 ± 1.54)	(14.39 ± 1.34)	(2.40 ± 0.76)	(32.11 ± 1.76)	(94.76 ± 2.04)
			February	(1.36 ± 0.18)	(1.73 ± 0.11)	(4.13 ± 0.19)	(2.56 ± 0.24)	(1.09 ± 0.17)	(24.85 ± 0.25)	(35.84 ± 0.19)
			April	(3.78 ± 0.97)	(53.49 ± 2.89)	(18.49 ± 2.96)	(83.21 ± 3.94)	(5.47 ± 1.32)	(252.52 ± 3.62)	(416.97 ± 10.84)
			July	(1.10 ± 0.11)	(1.51 ± 0.29)	(3.27 ± 0.20)	(1.84 ± 0.17)	(0.31 ± 0.10)	(4.12 ± 0.23)	(12.24 ± 0.16)
			November	(8.54 ± 0.88)	(11.80 ± 2.29)	(25.52 ± 1.54)	(14.39 ± 1.34)	(2.40 ± 0.76)	(32.11 ± 1.76)	(94.76 ± 2.04)
			February	(1.36 ± 0.18)	(1.73 ± 0.11)	(4.13 ± 0.19)	(2.56 ± 0.24)	(1.09 ± 0.17)	(24.85 ± 0.25)	(35.84 ± 0.19)

ATR: atrazine; DIHA: desisopropylhydroxyatrazine; DEHA: desethylhydroxyatrazine; DIA: desisopropylatrazine; DEA: desethylatrazine; HA: hydroxyatrazine.

Table 2

Description of the sampling sites and mean concentrations (\pm standard deviations) of ATR and its metabolites in the April 2018 sediment sampling campaign of the Volturno River, southern Italy.

Sampling location			Compound (ng g ⁻¹ dw)						
Site number identification	Site characteristics	Site location	ATR	DIHA	DEHA	DIA	DEA	HA	Total
1 (river water)	Volturno River mouth	41°01'19"N 13°55'26"E	4.25 \pm 0.29	1.57 \pm 0.31	2.93 \pm 0.19	1.36 \pm 0.32	3.12 \pm 0.23	5.11 \pm 0.17	18.59 \pm 0.46
2 (seawater)	River mouth 500 m north	41°01'05"N 13°55'38"E	3.37 \pm 0.28	0.57 \pm 0.12	1.75 \pm 0.31	0.83 \pm 0.19	1.91 \pm 0.16	3.68 \pm 0.24	12.50 \pm 0.65
3 (seawater)	River mouth 1000 m north	41°00'51"N 13°55'48"E	2.26 \pm 0.16	0.26 \pm 0.08	1.39 \pm 0.19	0.70 \pm 0.17	0.93 \pm 0.10	2.09 \pm 0.12	7.73 \pm 0.16
4 (seawater)	River mouth 1500 m north	41°00'33"N 13°55'49"E	1.53 \pm 0.03	nd	1.07 \pm 0.04	0.11 \pm 0.00	0.75 \pm 0.12	1.16 \pm 0.03	4.61 \pm 0.13
5 (seawater)	River mouth 500 m west	41°01'25"N 13°55'56"E	3.96 \pm 0.17	0.62 \pm 0.30	1.96 \pm 0.12	1.04 \pm 0.08	2.40 \pm 0.21	3.94 \pm 0.18	13.93 \pm 0.53
6 (seawater)	River mouth 1000 m west	41°01'00"N 13°54'52"E	2.95 \pm 0.10	0.41 \pm 0.21	1.52 \pm 0.53	0.70 \pm 0.27	1.23 \pm 0.23	3.46 \pm 0.56	10.28 \pm 0.77
7 (seawater)	River mouth 1500 m west	41°00'45"N 13°54'40"E	2.52 \pm 0.54	0.27 \pm 0.07	1.29 \pm 0.19	0.14 \pm 0.03	2.01 \pm 0.16	2.51 \pm 0.61	8.75 \pm 1.20
8 (seawater)	River mouth 500 m south	41°01'30"N 13°55'10"E	4.14 \pm 0.16	1.19 \pm 0.20	2.10 \pm 0.14	1.28 \pm 0.48	2.94 \pm 0.46	4.47 \pm 1.04	16.11 \pm 1.10
9 (seawater)	River mouth 1000 m south	41°01'47"N 13°55'05"E	3.95 \pm 0.48	0.76 \pm 0.25	1.81 \pm 0.47	1.18 \pm 0.06	2.45 \pm 0.49	3.53 \pm 0.63	13.69 \pm 1.79
10 (seawater)	River mouth 1500 m south	41°02'02"N 13°54'56"E	3.68 \pm 0.71	0.54 \pm 0.20	1.76 \pm 0.25	0.75 \pm 0.45	1.65 \pm 0.16	3.30 \pm 0.62	11.67 \pm 0.57

ATR: atrazine; DIHA: desisopropylhydroxyatrazine; DEHA: desethylhydroxyatrazine; DIA: desisopropylatrazine; DEA: desethylatrazine; HA: hydroxyatrazine; nd: Not detected.

concentrations detected in SPM and SED ($[SPM]/[SED]$) were evaluated. In both cases, the ratios were > 1 , for all sites and for all sampling seasons. Therefore, the concentrations of these pollutants decreased from WDP to SPM and more to SED. In sediment samples the highest concentrations were related to HA, which is more adsorbed than others metabolites because of its relatively low water solubility (3.9 mg/L), its longest half-life in soil (164 days) and its high adsorption coefficient ($K_f = 25 \mu\text{mol L}^{-1}\text{Kg}^{-1}$), followed by ATR with a lower coefficient ($K_f = 3.7 \mu\text{mol L}^{-1}\text{kg}^{-1}$) (Barchanska et al., 2017; Mersie and Seybold, 1996). The persistence of ATR could be due both to the high amount applied annually in the past and to the ability to establish strong bonds with the organic colloids present in the clayey fraction of the soil. This determines the slow and continuous release of the herbicide and its presence has even been detected in waters even after years of its use. Another reason that contributes to increasing the environmental persistence of ATR is due to the difficulty of organisms in metabolizing these substances. Some studies showed that *Pseudomonas* sp. strain ADP is able to metabolize ATR and this led to the use of this organism in programs of decontamination of ATR-polluted sites (Govantes et al., 2010; Jablonowski et al., 2011). Compared to concentrations found in other countries (Table 3), in some of which the ATR is still sold and used, the concentrations obtained for ATR and its metabolites in the Volturno River estuary are significantly low for both water and sediment samples.

To study the relationship between WDP, SPM and sediment a SEM has been constructed. Through this model, two hypotheses were proposed: hypothesis H1, the pollution contained in the sediment was transmitted directly to the WDP; hypothesis H2, the pollution of the sediment is transmitted to the WDP through the SPM. Starting from this consideration, it has been hypothesized that sediment and SPM were exogenous latent variables (LVs) while WDP was an endogenous LV. Following the criteria summarized in Sarnacchiaro and Boccia (2018), it was supposed that all latent variables were reflective. The results of the PLS estimations on the model are presented in Fig. 4. Regarding the relationship among sediment, SPM and WDP we pointed out that the coefficient between sediment and SPM and between SPM and WDP were statistically significant. On the other side the coefficient between sediment and WDP was not statistically significant. Thus, the hypothesis H2 was confirmed and the relationship between sediment and WDP pollutants occurs through the SPM. These results suggest that SPM

presumably acts as a carrier of ATR and its metabolites from sediment to WDP.

3.2. Spatial-temporal distribution and load into the Mediterranean Sea

The total load contribution of ATR and metabolites to the central Mediterranean Sea from the Volturno River mouth was determined by the product of the flow-averaged mean concentration and the total river discharge. The flow-averaged mean concentrations were calculated as the sum of the products between the instantaneous total concentrations and water flow discharges, calculated by means of daily averaged water flow. The total load contribution was calculated in about $30.4 \text{ kg year}^{-1}$.

The inputs mainly occurred at the river mouth by diffuse surface or subsurface hydrological pathways, including storm water runoff and tributary inflow. In detail, the load was about $2.52 \text{ kg year}^{-1}$ for ATR, $2.72 \text{ kg year}^{-1}$ for DIHA, $3.98 \text{ kg year}^{-1}$ for DEHA, $3.80 \text{ kg year}^{-1}$ for DIA, $1.57 \text{ kg year}^{-1}$ for DEA, $15.84 \text{ kg year}^{-1}$ for HA. These results suggest that although the concentrations of individual analytes are relatively low, the Volturno River certainly represented an important point source discharge of these pollutants into Central Mediterranean Sea.

The ATR and metabolites load in the Volturno River were compared with other rivers worldwide. The loads in the Volturno River were lower than Yangtze River (China) by Qi et al., 2014 for ATR, DEA DIA and HA (10,000, 2600, 4800 and 25,400 kg year^{-1} respectively), St. Lawrence River (Canada) by Montiel-León et al., 2019 and Elbe River (Europe) by Karlsson et al., 2020 for ATR (3000 and 73.2 kg year^{-1} respectively). It should be highlighted that this study is the first to evaluate the ATR and metabolites discharge in the Central Mediterranean Sea from the Volturno River and for this reason it is not possible to compare with previous data in the same research area.

The spatial distribution of ATR and DPs from the Volturno River was evaluated by comparing the amount of the samples collected in 10 sampling sites and in four seasons, with rain and without rain. The results are shown in Fig. 5 where it could be observed that the highest concentrations levels were found for WDP at the river mouth (105.55 ng L^{-1} in February) and gradually decreased from 59.04 ng L^{-1} (mean value of four seasons) at 500 m, to 51.31 ng L^{-1} (mean value of four seasons) at 1000 m and 45.41 ng L^{-1} (mean value of four seasons) at 1500 m southward, probably because of a dilution effect by marine waters.

Table 3

Concentration ranges of ATR and its metabolites in water dissolved phase WDP (ng L^{-1}) and suspended particulate matter SPM (ng g^{-1}), from recent studies of different rivers, estuaries and coasts in the world.

Area	ATR	DEA	DIA	DEHA	DIHA	HA	References
Water dissolved phase (WDP)							
Asia							
Liao River system, China	65.5-1513	ND-47.1	ND-85.2				Gfrerer et al. (2002)
Jelum River, Pakistan	146-150.3						Maqbool et al. (2008)
Ravi River, Pakistan	ND-14.3						Maqbool et al. (2008)
Chenab River, Pakistan	ND-9.3						Maqbool et al. (2008)
Henan Province, China	10-8060	10-2300	ND			50-3400	Yu et al. (2018)
Baima River, China	10-1120	1960-2330	260				Sun et al. (2019)
Liaodong Peninsula, China	8.7-64.8						Xie et al. (2019)
Hong Kong, China	5.73	2.06	0.70			1.04	Wang et al. (2020)
America							
Mundaú-Manguba, Brazil	0.7-3.1						Azevedo et al. (2010)
Lucas do Rio Verde, Brazil	ND-4920	ND-1260					Nogueira et al. (2012)
Potomac River, USA	71	81					Kolpin et al. (2013)
Mista stream basin, Argentina	88-324						De Geronimo et al. (2014)
Pardo River, Brazil	160-180						Machado et al. (2017)
Elkhorn River, USA	1990	220	30				Ali et al. (2018)
Cachapoal River, Chile	ND-149	ND-48	ND-154	ND-485	ND-803	ND-84	Climent et al. (2019)
Paraná Basin, Brazil	ND-2890	ND-800	ND-1120				Della Flora et al. (2019)
Africa							
Mefou River, Cameroon	ND-460.7	ND	ND-4.5				Branchet et al. (2018)
Crocodile River, South Africa	483-940	106-184	10-22			2-4	Rimayi et al. (2018)
Magalies River, South Africa	234-830	19-162	2-14			1-4	Rimayi et al. (2018)
Australia							
Mary River, Australia	ND-110						McMahon et al. (2005)
Barratta Creek River, Australia	13,000						Wood et al. (2017)
Europe							
Scheldt River, Netherlands	750	100-200					Steen et al. (2001)
Danube River, Hungary	0.4	ND	ND			0.35	Takáts et al. (2001)
Scheldt River, Belgium	ND-626						Noppe et al. (2007)
Duero River, Spain	10-630	10-120					Hildebrandt et al. (2008)
Mino River, Spain	20-70						Hildebrandt et al. (2008)
Billiers River, France	440	890	550				Caquet et al. (2013)
Baltic Sea, Germany	ND-2.1	ND-2.0	ND				Nödler et al. (2013)
Vannetin River, France	10-5200	50-2100	100-2800				Irace-Guigand et al. (2004)
Tejo River, Portugal	240	ND	ND				Silva et al. (2015)
Ria Formosa Lagoon, Portugal	ND-3.7	8.3-12.5					Cruzeiro et al. (2015)
Danube River, Serbia	4						Radović et al. (2015)
Tagus River, Portugal	382-550	14-101					Cruzeiro et al. (2016)
Klodnica River, Poland	ND	ND	ND-11000			ND-35000	Barchanska et al. (2017)
Stream system, Germany	21	118	20				Weber et al. (2018)
Brittany River, France	ND	ND-51	ND				Gervais et al. (2008)
Mediterranean Sea							
Ebro River, Spain	12-170						Gómez-Gutiérrez et al. (2006)
Ebro River, Spain	194.9	160.9					Claver et al. (2006)
Sacca di Goro Lagoon, Italy	2.3-8.2	ND-4.1	ND-11.2	ND-14.9		ND-193.2	Carafa et al. (2007)
Ebro River, Spain	10-410	10-600					Hildebrandt et al. (2008)
Llobregat River, Spain	2.63-6.44						Masiá et al. (2015)
Ebro River, Spain	9	80	17			95	Benvenuto et al. (2010)
Ebro Delta, Spain	ND	ND	8			151	Benvenuto et al. (2010)
Verd River, Spain	4	9	10			ND	Benvenuto et al. (2010)
Ebro River, Spain	6-825	16-377					Navarro et al. (2010)
Northern Aegean Sea, Italy	1.6-15	ND-1.8	ND				Nödler et al. (2013)
Arno River, Italy	1.18						Bono and Magi (2013)
Po River, Italy	ND-90	ND-330					Ghirardelli et al. (2020)
Volturno River, Italy	0.13-8.22	0.77-6.34	2.31-10.79	1.12-13.18	1.26-9.35	12.07-59.32	This study
Suspended particulate matter (SPM)							
America							
Des Prairies River, Canada	55	9					Darwano et al. (2014)
Cachapoal River, Chile	ND	ND-5.67	ND	ND-425.1	ND-1123	58.5-1195	Climent et al. (2019)
Mediterranean Sea							
Volturno River, Italy	0.57-44.28	0.29-21.14	5.05-83.21	5.49-74.92	0.44-59.40	11.10-332.17	This study

ND: Not detected.

Considering period and sampling sites, an increase in the total concentration was observed in February, with the occurrence of precipitation and flooding events. This increase could be explained probably

due to ATR capability to remain in the sediment for a long time and remobilize through resuspension events and runoff (Carafa et al., 2007; Climent et al., 2019; Vonberg et al., 2014b). The results obtained are in

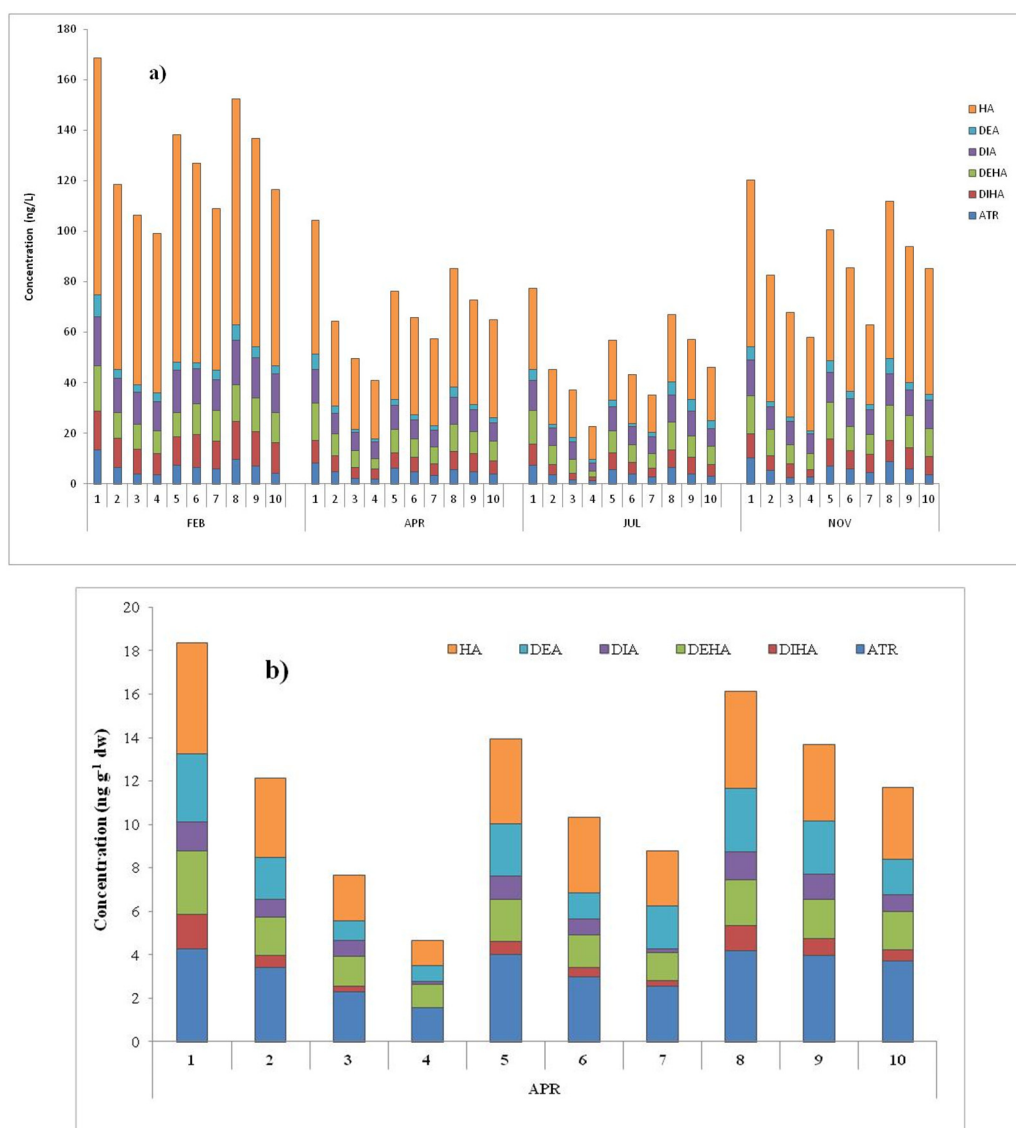


Fig. 3. a) Concentration of atrazine and its metabolites (ng L^{-1}) detected **a)** in water (WDP + SPM) of the Volturno River estuary in four seasons (February, April, July and November) and **b)** in sediment samples (ng g^{-1} dry wt) in April in 10 sampling sites (1: River Mouth; 2: North estuary at 500 m; 3: North estuary at 1000 m; 4: North estuary at 1500 m; 5: West estuary at 500 m; 6: West estuary at 1000 m; 7: West estuary at 1500 m; 8: South estuary at 500 m; 9: South estuary at 1000 m; 10: South estuary at 1500 m).

agreement with those found by Carafa et al. (2007) in Sacca di Goro (Italy) observing a random distribution of analytes concentrations with a peak of HA amount during the winter campaign. Likewise, our results match with those found at the Mato Grosso (Brazil) (Dores et al., 2008) and in the Hohra basin (France) (Grégoire et al., 2010), with the highest amount during the rainy season and during extreme rainfall-runoff episodes, respectively.

These results are also confirmed by the PCA, as observed in Fig. 6. PCA was conducted for the twelve variables in 10 water samples of four sampling campaigns. The Eigenvalues and the cumulative proportions of the explained variance suggest that it is reasonable to retain the first two PCs. In fact, the first 2 PCs explain up to 81.5% of the total variability. The plot of the first two PCs against each other (Fig. 6a) enhances visual interpretation. The first factor (PC1, 64,2%) represents mainly the variables of WDP, the second (PC2, 17,3%) represents the variables of SPM. Looking at the plot of the first two principal components, it was observed that the first component points out a greater concentration of the WDP variables in all the sites during the month of February, in particular at the sites Volturno River mouth (1feb) and at 500 m South (8feb). The second component highlights higher concentration of SPM variables during November, also in this case the most

polluted sites are Volturno River mouth (1nov) and at 500 m South (8nov) (Fig. 6b).

The concentrations of ATR and its DPs found in the present study are in accordance with those reported by other studies carried out in Europe after ATR was finally banned in 2004. Caquet et al. (2013) estimated the amount of this herbicide in France and they confirm that these compounds were frequently found in surface water, while Vonberg et al. (2014b) explained that although ATR was banned in 1991 in Germany, the concentrations of these pesticides exceed threshold values. The presence of ATR and its DPs were investigated in several studies in Italy. Guzzella et al. (2006) and Loos et al. (2007) evaluated the presence of these analytes in Northern Italy and DEA and DIA were found in most of the samples analyzed. Carafa et al. (2007) estimated ATR and metabolites in surface water and in sediment samples collected in Sacca di Goro coastal lagoon, located in the Southern part of the Po River Delta and connected to the Northern Adriatic Sea. According to their study, ATR and its DPs were detected in many water samples, with a predominance of HA due to the release of herbicide residual from sediment. Previous studies in water samples from Italy and Spain (Benvenuto et al., 2010; Rousis et al., 2017) indicated the presence of herbicides in quantifiable concentrations. Cruzeiro et al. (2016)

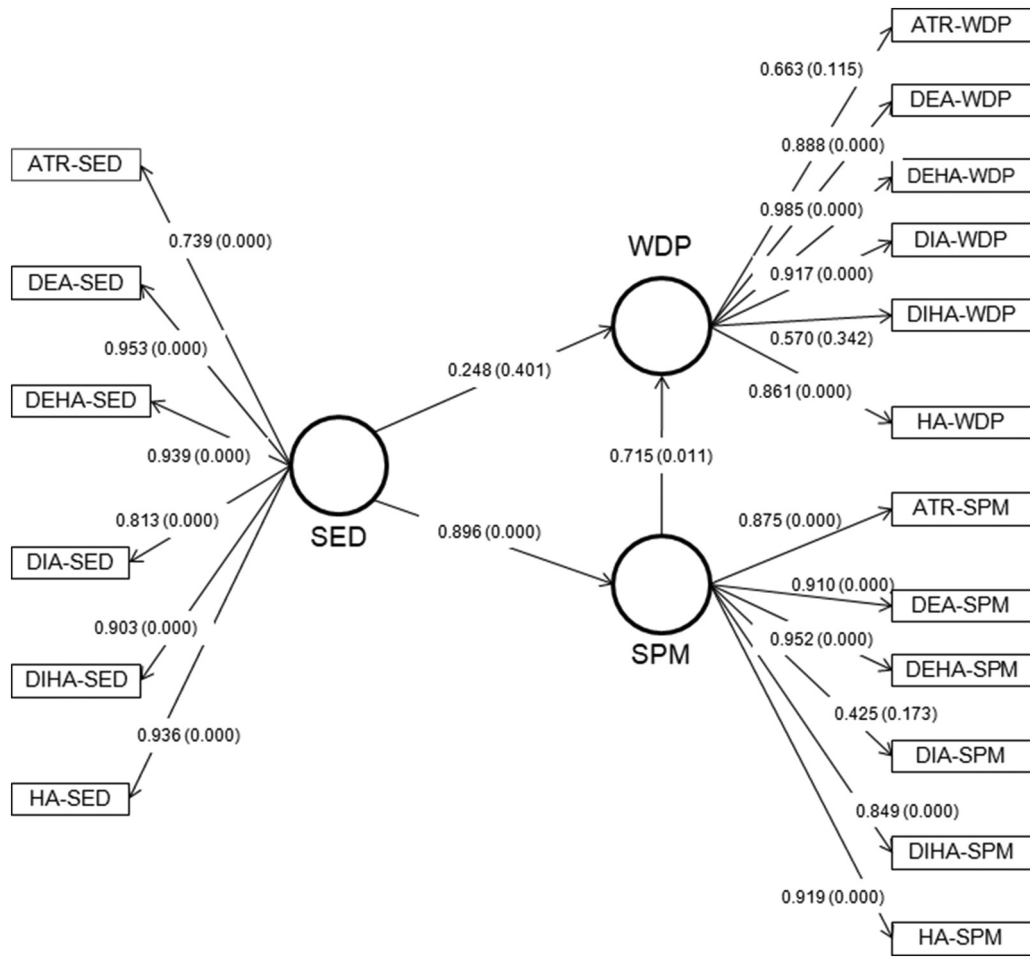


Fig. 4. Structural equation model: path coefficients and *p*-values (Latent constructs are shown with a circle and measured variables are shown with a rectangle).

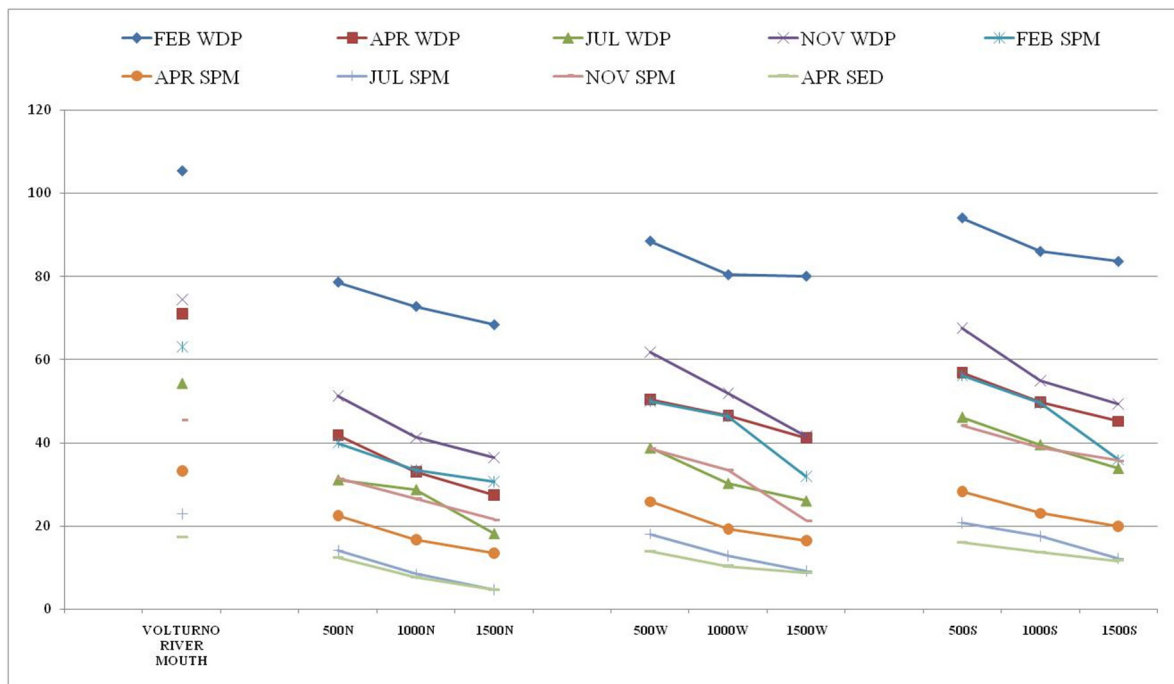


Fig. 5. Spatial and temporal concentration of atrazine and its metabolites in the water dissolved phase (WDP, ng L⁻¹), the suspended particulate matter (SPM, ng L⁻¹) and the sediments (SED, ng g⁻¹ dry wt) of the Volturno River, southern Italy.

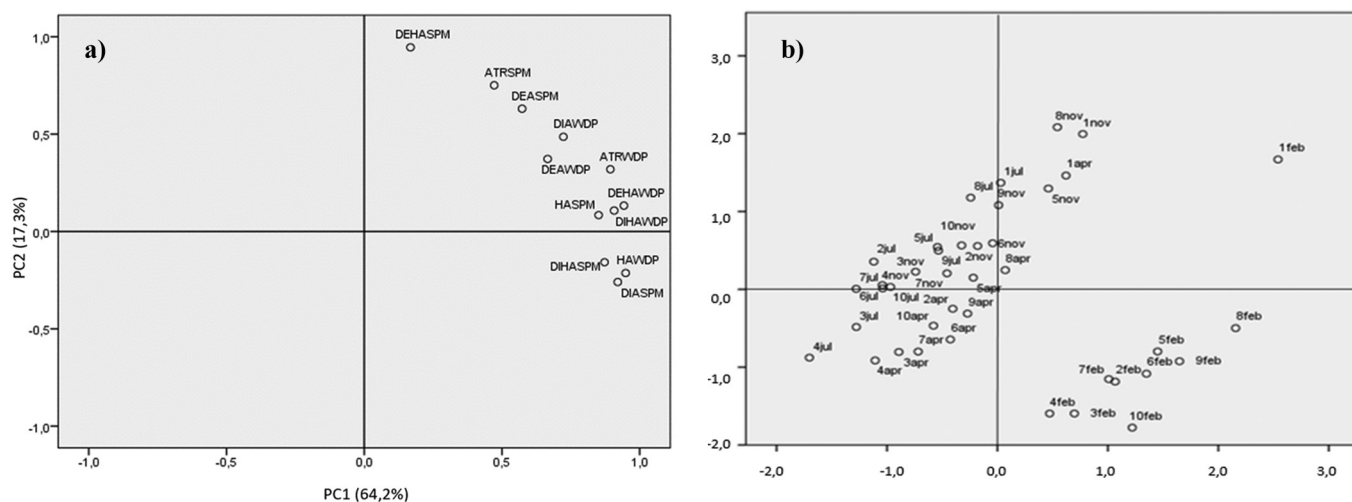


Fig. 6. Principal Component Analysis (PCA) of the water dissolved phase (WDP) and suspended particulate matter (SPM) data of the Voltorno River **a)** Loading plot of the two components influencing atrazine and its metabolites in the aquatic environment; **b)** Score plot for the first and second principal component.

determined DEA in the Mondego River estuary (Portugal) in surface water samples and the concentrations were always above the limits established by the European Directive 98/83/EC (European Commission Council Directive 98/83/EC). Barchanska et al. (2017) assessed the behavior of these pesticides in water and sediment from Klodnika River (Poland), observing that in all samples ATR was not present while DEA, DIA and HA were found in water and sediment samples. However, the concentrations of these compounds were significantly higher than in the present report.

3.3. Metabolite to parent ratio

Some ATR metabolites were studied in this paper and among these DEA, DIA and HA are identified as key metabolites. In particular, Directive 91/414/EEC (Directive, C., 1991) classified DEA and DIA as “relevant” metabolites of ATR (Vonberg et al., 2014a). In fact, DEA and DIA have a chemical structure and a toxicological profile similar to that of ATR (Ralston-Hooper et al., 2009), while HA has a different action mode than the parental compound and it is toxic mainly to the kidneys (Krutz et al., 2010). Moreover, chlorinated DPs are formed in the sediment only if ATR has sufficient residence time to be N-dealkylated by microbial activity, however HA can form in the sediment both in abiotic and biotic conditions and therefore its presence could not be interpreted unambiguously.

The desethylatrazine-to-atrazine ratio (DAR) is used to assess the slow rate of ATR mobility from sediment to water and it may be useful for characterizing point and nonpoint- source contamination of ATR (Ghirardelli et al., 2020). The DAR was determined using:

$$DAR = [DEA]/[ATR] \quad (3)$$

DAR values <0.5 indicate a point-source contamination and a relatively short contact time between ATR and the sediment microorganisms, while DAR values >0.5 suggest a longer residence time of ATR in sediment and exclude external point sources (Lerch and Willett, 2019; Ghirardelli et al., 2020).

The results in the Voltorno River showed values >0.5 for all samples analyzed and this suggest that ATR was derived from historical discharge, indicating a long persistence in the environment and a nonpoint-source contamination. The results of this study are consistent with Vonberg et al. (2014a) and Ghirardelli et al. (2020), which evaluated the trends in ATR and DEA concentrations in aquifers over several years and observed constant values of DAR.

4. Conclusions

The intensive use of pesticides has caused concern among authorities in different countries, as many of them are not easily degradable and remain unchanged for a long time, consequently threatening environmental sustainability. In view of this, monitoring programmes are needed in order to assess the environmental impact and protect the quality of water and land resources. This study is the first to offer helpful information about the levels regarding ATR and its DPs contamination in the Voltorno River estuary. The results indicate that higher levels of ATR and its DPs were found in water (as sum of WDP + SPM) than in sediment samples, due to their physico-chemical properties such as relatively high solubility in water, low adsorption to sediment and high persistence in the environment. The data regarding the spatial and seasonal distribution showed higher pollution levels near the river mouth, in particular at 500 m southward and in the winter period due to increased rainfall. The findings also suggested that the contaminants load was heading South into the Mediterranean Sea. The DAR ratio between DEA and ATR was always >0.5 suggesting an historical discharge and classifies ATR as a nonpoint source contaminant. This study is the first to investigate the levels of ATR in water and sediments of southern Italy, despite being banned many years ago. Besides providing the state of pollution of this river, this research shows its environmental impact on the Mediterranean Sea and offers useful data for national legislation and standards on water contaminants.

CRedit authorship contributions statement

M.T., P.M. and S.D. designed the research; P.M., D.P.P., E.D. and F.D. organized and carried out samplings and laboratory analyzes; P.S., P.M. and E.D. analyzed the data and performed the statistical analysis. All authors have discussed results and co-written the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2021.149972>.

References

- Ali, J.M., D'Souza, D.L., Schwarz, K., Allmon, L.G., Singh, R.P., Snow, D.D., Bartelt-Hunt, S.L., Kolok, A.S., 2018. Response and recovery of fathead minnows (*Pimephales promelas*) following early life exposure to water and sediment found within agricultural runoff from the Elkhorn River, Nebraska, USA. *Sci. Total Environ.* 618, 1371–1381. <https://doi.org/10.1016/j.scitotenv.2017.09.259>.
- Almasi, H., Takdastan, A., Jaafarzadeh, N., Babaei, A.A., Birgani, Y.T., Cheraghian, B., Jorfi, S., 2020. Spatial distribution, ecological and health risk assessment and source identification of atrazine in Shadegan international wetland, Iran. *Mar. Pollut. Bull.* 160, 111569. <https://doi.org/10.1016/j.marpolbul.2020.111569>.
- Azevedo, D.A., Silva, T.R., Knoppers, B.A., Schulz-Bull, D., 2010. Triazines in the tropical lagoon system of Mundaú-Manguaba, NE-Brazil. *J. Braz. Chem. Soc.* 21 (6), 1096–1105. <https://doi.org/10.1590/S0103-50532010000600020>.
- Barchanska, H., Sajdak, M., Szczypka, K., Swientek, A., Tworek, M., Kurek, M., 2017. Atrazine, triketone herbicides, and their degradation products in sediment, soil and surface water samples in Poland. *Environ. Sci. Pollut. Res.* 24, 644–658. <https://doi.org/10.1007/s11356-016-7798-3>.
- Battaglin, W.A., Bradley, P.M., Iwanowicz, L., Journey, C.A., Walsh, H.L., Blazer, V.S., 2018. Pharmaceuticals, hormones, pesticides, and other bioactive contaminants in water, sediment, and tissue from Rocky Mountain National Park, 2012–2013. *Sci. Total Environ.* 643, 651–673. <https://doi.org/10.1016/j.scitotenv.2018.06.150>.
- Benvenuto, F., Marín, J.M., Sancho, J.V., Canobbio, S., Mezzanotte, V., Hernández, F., 2010. Simultaneous determination of triazines and their main transformation products in surface and urban wastewater by ultra-high-pressure liquid chromatography-tandem mass spectrometry. *Anal. Bioanal. Chem.* 397 (7), 2791–2805. <https://doi.org/10.1007/s00216-010-3712-x>.
- Bono, L., Magi, E., 2013. Fast and selective determination of pesticides in water by automated on-line solid phase extraction liquid chromatography tandem mass spectrometry. *Anal. Lett.* 46 (10), 1467–1476. <https://doi.org/10.1080/00032719.2013.769263>.
- Branchet, P., Cadot, E., Fenet, H., Sebagn, D., NgonounNgatcha, B., Borrell-Estupina, V., Remy Ndamngoupayou, J., Kengne, I., Braum, J., Gonzalez, C., 2018. Polar pesticide contamination of an urban and peri-urban tropical watershed affected by agricultural activities (Yaoundé, Center Region, Cameroon). *Environ. Sci. Pollut. Res.* 25, 17690–17715. <https://doi.org/10.1007/s11356-018-1798-4>.
- Caquet, Th., Roucaute, M., Mazzella, N., Delmas, F., Madigou, C., Farcy, E., Burgeot, Th., Allenou, J.-P., Gabellec, R., 2013. Risk assessment of herbicides and booster biocides along estuarine continuums in the Bay of Vilaine area (Brittany, France). *Environ. Sci. Pollut. Res.* 20, 651–666. <https://doi.org/10.1007/s11356-012-1171-y>.
- Carafa, R., Wollgast, J., Canuti, E., Ligthart, J., Dueri, S., Hanke, G., Eisenreich, S.J., Viaroli, P., Zaldívar, J.M., 2007. Seasonal variations of selected herbicides and related metabolites in water, sediment, seaweed and clams in the Sacca di Goro coastal lagoon (Northern Adriatic). *Chemosphere* 69, 1625–1637. <https://doi.org/10.1016/j.chemosphere.2007.05.060>.
- Cardeal, Z.L., Souza, A.G., Amorim, L.C., 2011. *Analytical Methods for Performing Pesticide Degradation Studies in Environmental Samples*. IntechOpen.
- Claver, A., Ormad, P., Rodríguez, L., Ovelleiro, J.L., 2006. Study of the presence of pesticides in surface waters in the Ebro River basin (Spain). *Chemosphere* 64, 1437–1443. <https://doi.org/10.1016/j.chemosphere.2006.02.034>.
- Climent, M.J., Sánchez-Martín, M.J., Rodríguez-Cruz, M.S., Pedreros, P., Urrutia, R., Herrero-Hernández, E., 2018. Determination of pesticides in river surface waters of Central Chile using SPE-GC-MS multi-residue method. *J. Chil. Chem. Soc.* 63 (2), 4023–4031. <https://doi.org/10.4067/s0717-97072018000204023>.
- Climent, M.J., Herrero-Hernández, E., Sánchez-Martín, M.J., Rodríguez-Cruz, M.S., Pedreros, P., Urrutia, R., 2019. Residues of pesticides and some metabolites in dissolved and particulate phase in surface stream water of Cachapoal River basin, central Chile. *Environ. Pollut.* 251, 90–101. <https://doi.org/10.1016/j.envpol.2019.04.117>.
- Commission Decision 2004/248/EC, 2004. Commission decision of 10 March 2004 concerning the non-inclusion of atrazine in Annex 1 to Council Directive 91/414/EEC and the withdraw of authorisation for plant protection products containing this active substance. *Off. J. Eur. Union* L78, 53–55.
- Corcoran, S., Metcalfe, C.D., Sultana, T., Amé, M.V., Menone, M.L., 2020. Pesticides in surface waters in Argentina monitored using polar organic chemical integrative samplers. *Bull. Environ. Contam. Toxicol.* 104 (1), 21–26. <https://doi.org/10.1007/s00128-019-02758-z>.
- Cruzeiro, C., Pardo, M.Á., Rocha, E., Rocha, M.J., 2015. Occurrence and seasonal loads of pesticides in surface water and suspended particulate matter from a wetland of worldwide interest—the Ria Formosa Lagoon, Portugal. *Environ. Monit. Assess.* 187 (11), 669. <https://doi.org/10.1007/s10661-015-4824-8>.
- Cruzeiro, C., Pardo, M.Á., Rodrigues-Oliveira, N., Castro, L.F.C., Rocha, E., Rocha, M.J., 2016. Multi-matrix quantification and risk assessment of pesticides in the longest river of the Iberian Peninsula. *Sci. Total Environ.* 572, 263–272. <https://doi.org/10.1016/j.scitotenv.2016.07.203>.
- Cui, Y., Yin, K., Gong, Y., Qu, Y., Liu, H., Lin, H., 2019. Atrazine induces necroptosis by miR-181-5p targeting inflammation and glycometabolism in carp lymphocytes. *Fish Shellfish Immunol.* 94, 730–738. <https://doi.org/10.1016/j.fsi.2019.09.068>.
- Darwano, H., Vo Duy, S., Sauve, S., 2014. A new protocol for the analysis of pharmaceuticals, pesticides, and hormones in sediments and suspended particulate matter from rivers and municipal wastewaters. *Arch. Environ. Contam. Toxicol.* 66, 582–593. <https://doi.org/10.1007/s00244-014-0007-9>.
- De Geronimo, E., Aparicio, V.C., Bárbaro, S., Portocarrero, R., Jaime, S., Costa, J.L., 2014. Presence of pesticides in surface water from four sub-basins in Argentina. *Chemosphere* 107, 423–431. <https://doi.org/10.1016/j.chemosphere.2014.01.039>.
- Della Flora, A., Wielens Becker, R., FrederigiBenassi, S., Toci, A.T., Cordeiro, G.A., Ibáñez, M., Portolés, T., Hernández, F., Boroski, M., Sirtori, C., 2019. Comprehensive investigation of pesticides in Brazilian surface water by high resolution mass spectrometry screening and gas chromatography– mass spectrometry quantitative analysis. *Sci. Total Environ.* 669, 248–257. <https://doi.org/10.1016/j.scitotenv.2019.02.354>.
- Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. *Off. J. Eur. Communities*, L226, 1–17.
- Directive, C., 1991. Council Directive 91/414/EEC of 15 July 1991 concerning the placing of plant protection products on the market. *Off. J. Eur. Commun.* L 230, 1–32.
- Dores, E.F., Carbo, L., Ribeiro, M.L., De-Lamonica-Freire, E.M., 2008. Pesticide levels in ground and surface waters of Primavera Do Leste Region, Mato Grosso, Brazil. *J. Chromatog. Sci.* 46 (7), 585–590. <https://doi.org/10.1093/chromsci/46.7.585>.
- Esposito, F., Nardone, A., Fasano, E., Scognamiglio, G., Esposito, D., Agrelli, D., Vanni, F., 2018. A systematic risk characterization related to the dietary exposure of the population to potentially toxic elements through the ingestion of fruit and vegetables from a potentially contaminated area. A case study: the issue of the "Land of Fires" area in Campania region, Italy. *Environ. Pollut.* 243, 1781–1790. <https://doi.org/10.1016/j.envpol.2018.09.058>.
- European Commission Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption.
- EUROSTAT, 2018. <https://ec.europa.eu/eurostat/en/web/products-eurostat-news/-/DDN-20181015-1>.
- Farlin, J., Gallé, T., Bayerle, M., Pittois, D., Braun, C., El Khabbaz, H., Weihermueller, L., 2013. Using the long-term memory effect of pesticide and metabolite soil residues to estimate field degradation half-life and test leaching predictions. *Geoderma* 207, 15–24. <https://doi.org/10.1016/j.geoderma.2013.04.028>.
- Farouni, A.I., Ngqwa, N.P., 2020. Occurrence of selected endocrine disrupting compounds in the eastern cape province of South Africa. *Environ. Sci. Pollut. Res.* 1–12. <https://doi.org/10.1007/s11356-020-08082-y>.
- Gervais, G., Brosillon, S., Laplanche, A., Helen, C., 2008. Ultra-pressure liquid chromatography–electrospray tandem mass spectrometry for multiresidue determination of pesticides in water. *J. Chromatogr. A* 1202, 163–172. <https://doi.org/10.1016/j.chroma.2008.07.006>.
- Gfrerer, M., Wenzl, T., Quan, X., Platzer, B., Lankmayr, E., 2002. Occurrence of triazines in surface and drinking water of Liaoning Province in Eastern China. *J. Biochem. Biophys. Methods* 53, 217–228. [https://doi.org/10.1016/S0165-022X\(02\)00110-0](https://doi.org/10.1016/S0165-022X(02)00110-0).
- Ghirardelli, A., Otto, S., Masin, R., Bano, C., Altissimo, L., Russo, S., Zanin, G., 2020. Thirty-year monitoring of s-triazine herbicide contamination in the aquifer north of Vicenza (north-east Italy). *Sci. Total Environ.* 752, 141647. <https://doi.org/10.1016/j.scitotenv.2020.141647>.
- Gilliom, R.J., Barbash, J.E., Crawford, C.G., Hamilton, P.A., Martin, J.D., Nakagaki, N., Wolock, D.M., 2006. *Pesticides in the Nation's Streams and Ground Water, 1992–2001* (No. 1291). US Geological Survey.
- Gómez-Gutiérrez, A., Jover, E., Bodineau, L., Albaige's, J., Bayona, J.M., 2006. Organic contaminant loads into the Western Mediterranean Sea: estimate of Ebro River inputs. *Chemosphere* 65, 224–236. <https://doi.org/10.1016/j.chemosphere.2006.02.058>.
- Gonsioroski, A., Mourikes, V.E., Flaws, J.A., 2020. Endocrine disruptors in water and their effects on the reproductive system. *Int. J. Mol. Sci.* 21 (6), 1929. <https://doi.org/10.3390/ijms21061929>.
- Govantes, F., García-González, V., Porrúa, O., Platero, A.I., Jiménez-Fernández, A., Santero, E., 2010. Regulation of the atrazine-degradative genes in *Pseudomonas* sp. strain ADP. *FEMS Microbiol. Lett.* 310 (1), 1–8. <https://doi.org/10.1111/j.1574-6968.2010.01991.x>.
- Grégoire, C., Payraudeau, S., Domange, N., 2010. Use and fate of 17 pesticides applied on a vineyard catchment. *Int. J. Environ. Anal. Chem.* 90 (3–6), 406–420. <https://doi.org/10.1080/03067310903131230>.
- Guzzella, L., Pozzoni, F., Giuliano, G., 2006. Herbicide contamination of surficial groundwater in northern Italy. *Environ. Pollut.* 142 (2), 344–353. <https://doi.org/10.1016/j.envpol.2005.10.037>.
- Hakoun, V., Orban, P., Dassargues, A., Brouyère, S., 2017. Factors controlling spatial and temporal patterns of multiple pesticide compounds in groundwater (Hesbaye chalk aquifer, Belgium). *Environ. Pollut.* 223, 185–199. <https://doi.org/10.1016/j.envpol.2017.01.012>.
- HELCOM, 1993. *Second Baltic Sea Pollution Load Compilation* Balt Sea Environ Proc no 45 Baltic Marine Environment Protection Commission (1993).
- Hildebrandt, A., Guillaumon, M., Lacorte, S., Tauler, R., Barceló, D., 2008. Impact of pesticides used in agriculture and vineyards to surface and groundwater quality (North Spain). *Water Res.* 42 (13), 3315–3326. <https://doi.org/10.1016/j.watres.2008.04.009>.
- Irace-Guigand, S., Aaron, J.J., Scribe, P., Barceló, D., 2004. A comparison of the environmental impact of pesticide multiresidues and their occurrence in river waters surveyed by liquid chromatography coupled in tandem with UV diode array detection and mass spectrometry. *Chemosphere* 55, 973–981. <https://doi.org/10.1016/j.chemosphere.2003.12.007>.
- Isidori, M., Lavorgna, M., Nardelli, A., Parrella, A., 2004. Integrated environmental assessment of Voltorno River in South Italy. *Sci. Total Environ.* 327, 123–134. <https://doi.org/10.1016/j.scitotenv.2004.01.021>.
- Jablonski, N.D., Schäffer, A., Burauel, P., 2011. Still present after all these years: persistence plus potential toxicity raise questions about the use of atrazine. *Environ. Sci. Pollut. Res.* 18, 328–331. <https://doi.org/10.1007/s11356-010-0431-y>.
- Jiang, Z., Li, J., Jiang, D., Gao, Y., Chen, Y., Wang, W., Zhang, Y., 2020. Removal of atrazine by biochar-supported zero-valent iron catalyzed persulfate oxidation: reactivity, radical production and transformation pathway. *Environ. Res.* 184, 109260. <https://doi.org/10.1016/j.envres.2020.109260>.
- Jöreskog, K.G., 1970. A general method for estimating a linear structural equation system. *ETS Res. Rep. Ser.* 1970 (2). <https://doi.org/10.1002/j.2333-8504.1970.tb00783.x>.
- Karlsson, A.S., Lesch, M., Weihermüller, L., Thiele, B., Disko, U., Hofmann, D., Spielvogel, S., 2020. Pesticide contamination of the upper Elbe River and an

- adjacent floodplain area. *J. Soils Sediments* 1–15. <https://doi.org/10.1007/s11368-020-02571-w>.
- Köck-Schulmeyer, M., Olmos, M., López de Alda, M., Barceló, D., 2013. Development of a multiresidue method for analysis of pesticides in sediments based on isotope dilution and liquid chromatography–electrospray–tandem mass spectrometry. *J. Chromatogr. A* 1305, 176–187. <https://doi.org/10.1016/j.chroma.2013.07.036>.
- Kolpin, D.W., Blazer, V.S., Gray, J.L., Focazio, M.J., Young, J.A., Alvarez, D.A., Iwanowicz, L.R., Foreman, W.T., Furlong, E.T., Speiran, G.K., Zaugg, S.D., Hubbard, L.E., Meyer, M.T., Sandstrom, M.W., Barber, L.B., 2013. Chemical contaminants in water and sediment near fish nesting sites in the Potomac River basin: determining potential exposures to smallmouth bass (*Micropterus dolomieu*). *Sci. Total Environ.* 443, 700–716. <https://doi.org/10.1016/j.scitotenv.2012.09.063>.
- Krutz, L.J., Shaner, D.L., Zablutowicz, R.M., 2010. Enhanced degradation and soil depth effects on the fate of atrazine and major metabolites in Colorado and Mississippi soils. *J. Environ. Qual.* 39 (4), 1369–1377. <https://doi.org/10.2134/jeq2009.0197>.
- Le Coadou, L., Le Ménach, K., Labadie, P., Dévier, M.H., Pardon, P., Augagneur, S., Budzinski, H., 2017. Quality survey of natural mineral water and spring water sold in France: monitoring of hormones, pharmaceuticals, pesticides, perfluoroalkyl substances, phthalates, and alkylphenols at the ultra-trace level. *Sci. Total Environ.* 603, 651–662. <https://doi.org/10.1016/j.scitotenv.2016.11.174>.
- Lerch, R.N., Willett, C.D., 2019. Chloro-triazine transport to streams—evaluating methods for partitioning deisopropylatrazine sources. *Sci. Total Environ.* 697, 133931. <https://doi.org/10.1016/j.scitotenv.2019.133931>.
- Lerch, R.N., Groves, C.G., Polk, J.S., Miller, B.V., Shelley, J., 2018. Atrazine transport through a soil–epikarst system. *J. Environ. Qual.* 47 (5), 1205–1213. <https://doi.org/10.2134/jeq2017.12.0492>.
- Liu, J., Zhou, J.H., Guo, Q.N., Ma, L.Y., Yang, H., 2020. Physicochemical assessment of environmental behaviors of herbicide atrazine in soils associated with its degradation and bioavailability to weeds. *Chemosphere* 262, 127830. <https://doi.org/10.1016/j.chemosphere.2020.127830>.
- Loos, R., Wollgast, J., Huber, T., Hanke, G., 2007. Polar herbicides, pharmaceutical products, perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA), and nonylphenol and its carboxylates and ethoxylates in surface and tap waters around Lake Maggiore in northern Italy. *Anal. Bioanal. Chem.* 387 (4), 1469–1478. <https://doi.org/10.1007/s00216-006-1036-7>.
- Machado, C.S., Fregonesi, B.M., Alves, R.I.S., Tonani, K.A.A., Sierra, J., Martinis, B.S., Celere, B., Mari, Montse, Schuhmacher, M., Nadal, M., Domingo, Jose L., J.L., Segura-Muñoz, S., 2017. Health risks of environmental exposure to metals and herbicides in the Pardo River, Brazil. *Environ. Sci. Pollut. Res.* 24, 20160–20172. <https://doi.org/10.1007/s11356-017-9461-z>.
- Maqbool, U., Ul-Haq, A., Qureshi, M.J., 2008. Comparison of in-house-developed ELISA with HPLC techniques for the analysis of atrazine residues. *J. Environ. Sci. Health B* 43 (3), 224–230. <https://doi.org/10.1080/03601230701771131>.
- Masiá, A., Campo, J., Navarro-Ortega, A., Barceló, D., Picó, Y., 2015. Pesticide monitoring in the basin of Llobregat River (Catalonia, Spain) and comparison with historical data. *Sci. Total Environ.* 503, 58–68. <https://doi.org/10.1016/j.scitotenv.2014.06.095>.
- McMahon, K., Bengtson Nash, S., Eaglesham, G., Müller, J.F., Duke, N.C., Winderlich, S., 2005. Herbicide contamination and the potential impact to seagrass meadows in Hervey Bay, Queensland, Australia. *Mar. Pollut. Bull.* 51, 325–334. <https://doi.org/10.1016/j.marpolbul.2004.10.045>.
- Mersie, W., Seybold, C., 1996. Adsorption and desorption of atrazine, deethylatrazine, deisopropylatrazine, and hydroxyatrazine on levy wetland soil. *J. Agric. Food Chem.* 44 (7), 1925–1929. <https://doi.org/10.1021/jf950370k>.
- Montiel-León, J.M., Duy, S.V., Munoz, G., Bouchard, M.F., Amyot, M., Sauvé, S., 2019. Quality survey and spatiotemporal variations of atrazine and desethylatrazine in drinking water in Quebec, Canada. *Sci. Total Environ.* 671, 578–585. <https://doi.org/10.1016/j.scitotenv.2019.03.228>.
- Montuori and Triassi, 2012. Polycyclic aromatic hydrocarbons loads into the Mediterranean Sea: estimate of Sarno River inputs. *Mar. Pollut. Bull.* 64 (3), 512–520. <https://doi.org/10.1016/j.marpolbul.2012.01.003>.
- Navarro, A., Tauler, R., Lacorte, S., Barceló, D., 2010. Occurrence and transport of pesticides and alkylphenols in water samples along the Ebro River basin. *J. Hydrol.* 383 (1–2), 18–29. <https://doi.org/10.1016/j.jhydrol.2009.06.039>.
- Nödler, K., Licha, T., Voutsas, D., 2013. Twenty years later – atrazine concentrations in selected coastal waters of the Mediterranean and the Baltic Sea. *Mar. Pollut. Bull.* 70, 112–118. <https://doi.org/10.1016/j.marpolbul.2013.02.018>.
- Nogueira, E.N., Dores, E.F.G.C., Pinto, A.A., Amorim, R.S.S., Ribeiro, M.L., Lourencetti, C., 2012. Currently used pesticides in water matrices in central-western Brazil. *J. Braz. Chem. Soc.* 23 (8), 1476–1487. <https://doi.org/10.1039/C6EM00268D>.
- Noppe, H., Ghekiere, A., Verslycke, T., De Wulf, E., Verheyden, K., Monteyne, E., Polfliet, K., van Caeter, P., Janssen, C.R., De Brabander, H.F., 2007. Distribution and ecotoxicity of chlorotriazines in the Scheldt Estuary (B-NI). *Environ. Pollut.* 147, 668–676. <https://doi.org/10.1016/j.envpol.2006.09.016>.
- Ouyang, W., Zhang, Y., Gu, X., Tysklind, M., Lin, C., Wang, B., Xin, M., 2019. Occurrence, transportation, and distribution difference of typical herbicides from estuary to bay. *Environ. Int.* 130, 104858. <https://doi.org/10.1016/j.envint.2019.05.052>.
- Pose-Juan, E., Herrero-Hernández, E., Álvarez-Martín, A., Sánchez-Martín, M.J., Rodríguez-Cruz, M.S., 2014. Development of a procedure for the multiresidue analysis of pesticides in vineyard soils and its application to real samples. *J. Sep. Sci.* 37 (16), 2215–2224. <https://doi.org/10.1002/jssc.201400298>.
- Qi, W., Müller, B., Pernet-Coudrier, B., Singer, H., Liu, H., Qu, J., Berg, M., 2014. Organic micropollutants in the Yangtze River: seasonal occurrence and annual loads. *Sci. Total Environ.* 472, 789–799. <https://doi.org/10.1016/j.scitotenv.2013.11.019>.
- Qu, M., Li, N., Li, H., Yang, T., Liu, W., Yan, Y., Zhu, D., 2018. Phytoextraction and biodegradation of atrazine by *Myriophyllum spicatum* and evaluation of bacterial communities involved in atrazine degradation in lake sediment. *Chemosphere* 209, 439–448. <https://doi.org/10.1016/j.chemosphere.2018.06.055>.
- Radovic, T., Grujic, S., Petkovic, A., Dimkic, M., Laušević, M., 2015. Determination of pharmaceuticals and pesticides in river sediments and corresponding surface and ground water in the Danube River and tributaries in Serbia. *Environ. Monit. Assess.* 187, 4092. <https://doi.org/10.1007/s10661-014-4092-z>.
- Ralston-Hooper, K., Hardy, J., Hahn, L., Ochoa-Acuña, H., Lee, L.S., Mollenhauer, R., Sepúlveda, M.S., 2009. Acute and chronic toxicity of atrazine and its metabolites deethylatrazine and deisopropylatrazine on aquatic organisms. *Ecotoxicology* 18 (7), 899–905. <https://doi.org/10.1007/s10646-009-0351-0>.
- Rimayi, C., Odusanya, D., Weiss, J.M., de Boer, J., Chimuka, L., 2018. Seasonal variation of chloro-s-triazines in the Hartbeespoort Dam catchment, South Africa. *Sci. Total Environ.* 613, 472–482. <https://doi.org/10.1016/j.scitotenv.2017.09.119>.
- Rodríguez-González, N., Beceiro-González, E., González-Castro, M.J., Alpendurada, M.F., 2016. On-line solid-phase extraction method for determination of triazine herbicides and degradation products in seawater by ultra-pressure liquid chromatography–tandem mass spectrometry. *J. Chromatogr. A* 1470, 33–41. <https://doi.org/10.1016/j.chroma.2016.10.007>.
- Rousis, N.I., Bade, R., Bijlsma, L., Zuccato, E., Sancho, J.V., Hernandez, F., Castiglioni, S., 2017. Monitoring a large number of pesticides and transformation products in water samples from Spain and Italy. *Environ. Res.* 156, 31–38. <https://doi.org/10.1016/j.envres.2017.03.013>.
- Sarnacchiaro, P., Boccia, F., 2018. Some remarks on measurement models in the structural equation model: an application for socially responsible food consumption. *J. Appl. Stat.* 45 (7), 1193–1208. <https://doi.org/10.1080/02664763.2017.1363162>.
- Sassine, L., La Salle, C.L.G., Khaska, M., Verdoux, P., Meffre, P., Benfodda, Z., Roig, B., 2017. Spatial distribution of triazine residues in a shallow alluvial aquifer linked to groundwater residence time. *Environ. Sci. Pollut. Res.* 24 (8), 6878–6888. <https://doi.org/10.1007/s11356-016-7224-x>.
- Silva, E., Daam, M., Cerejeira, M.J., 2015. Aquatic risk assessment of priority and other river basin specific pesticides in surface waters of Mediterranean river basins. *Chemosphere* 135, 394–402. <https://doi.org/10.1016/j.chemosphere.2015.05.013>.
- Singh, S., Kumar, V., Chauhan, A., Datta, S., Wani, A.B., Singh, N., Singh, J., 2018. Toxicity, degradation and analysis of the herbicide atrazine. *Environ. Chem. Lett.* 16 (1), 211–237. <https://doi.org/10.1007/s10311-017-0665-8>.
- Singh, S., Kumar, V., Upadhyay, N., Singh, J., 2020. The effects of Fe (II), Cu (II) and humic acid on biodegradation of atrazine. *J. Environ. Chem. Eng.* 8 (2), 103539. <https://doi.org/10.1016/j.jece.2019.103539>.
- Steen, R., van der Vaart, J., Hiep, M., van Hattum, B., Cofino, W.P., Brinkman, U., 2001. Gross fluxes and estuary behavior of pesticides in the Scheldt Estuary (1995–1997). *Environ. Pollut.* 115, 65–79. [https://doi.org/10.1016/s0269-7491\(01\)00085-9](https://doi.org/10.1016/s0269-7491(01)00085-9).
- Sun, X., Liu, F., Fan, Y., Shan, R., 2019. Spatiotemporal distributions of Cu, Zn, metribuzin, atrazine, and their transformation products in the surface water of a small plain stream in eastern China. *Environ. Monit. Assess.* 191, 433. <https://doi.org/10.1007/s10661-019-7556-3>.
- Takáts, Z., Vargha, M., Vékey, K., 2001. Investigation of atrazine metabolism in river sediment by high-performance liquid chromatography/mass spectrometry. *Rapid Commun. Mass Spectrom.* 15 (18), 1735–1742. <https://doi.org/10.1002/rcm.425>.
- Toledo-Jaldin, H.P., Blanco-Flores, A., Sánchez-Mendieta, V., Martín-Hernández, O., 2018. Influence of the chain length of surfactant in the modification of zeolites and clays. Removal of atrazine from water solutions. *Environ. Technol.* 39 (20), 2679–2690. <https://doi.org/10.1080/09593330.2017.1365097>.
- Triassi, M., Nardone, A., Giovineti, M.C., De Rosa, E., Canzanella, S., Sarnacchiaro, P., Montuori, P., 2019. Ecological risk and estimates of organophosphate pesticides loads into the Central Mediterranean Sea from Volturno River, the river of the “Land of Fires” area, southern Italy. *Sci. Total Environ.* 678, 741–754. <https://doi.org/10.1016/j.scitotenv.2019.04.202>.
- UNEP and MAP, 2004. Guidelines for River (Including Estuary) Pollution Monitoring Programme for the Mediterranean Region MAP Technical Reports Series No 151. UNEP/MAP, Athens.
- Verde, R., Vigliotti, M., Prevedello, L., Sprovieri, M., Ruberti, D., 2013. An integrated approach to environmental quality assessment in a coastal setting in Campania (Southern Italy). *Environ. Earth Sci.* 70, 407–424. <https://doi.org/10.1007/s12665-012-2136-7>.
- Vonberg, D., Hofmann, D., Vanderborght, J., Lelickens, A., Köppchen, S., Pütz, T., Vereecken, H., 2014. Atrazine soil core residue analysis from an agricultural field 21 years after its ban. *J. Environ. Qual.* 43 (4), 1450–1459. <https://doi.org/10.2134/jeq2013.12.0497>.
- Vonberg, D., Vanderborght, J., Cremer, N., Pütz, T., Herbst, M., Vereecken, H., 2014. 20 years of long-term atrazine monitoring in a shallow aquifer in western Germany. *Water Res.* 50, 294–306. <https://doi.org/10.1016/j.watres.2013.10.032>.
- Wang, Q., Zhang, A., Li, P., Héroux, P., Zhang, H., Yu, X., Liu, Y., 2020. Degradation of aqueous atrazine using persulfate activated by electrochemical plasma coupling with microbubbles: removal mechanisms and potential applications. *J. Hazard. Mater.* 403, 124087. <https://doi.org/10.1016/j.jhazmat.2020.124087>.
- Wang, X., Jia, R., Song, Y., Wang, M., Zhao, Q., Sun, S., 2019. Determination of pesticides and their degradation products in water samples by solid-phase extraction coupled with liquid chromatography–mass spectrometry. *Microchem. J.* 149, 104013. <https://doi.org/10.1016/j.microc.2019.104013>.
- Weber, G., Christmann, N., Thiery, A.C., Martens, D., Kubiniok, J., 2018. Pesticides in agricultural headwater streams in southwestern Germany and effects on

- macroinvertebrate populations. *Sci. Total Environ.* 619–620, 638–648. <https://doi.org/10.1016/j.scitotenv.2017.11.155>.
- Wold, H., 1975. Path models with latent variables: the NIPALS approach. *Quantitative Sociology*, pp. 307–357.
- Wood, R.J., Mitrovic, S.M., Lim, R.P., Kefford, B.J., 2017. Chronic effects of atrazine exposure and recovery in freshwater benthic diatoms from two communities with different pollution histories. *Aquat. Toxicol.* 189, 200–208. <https://doi.org/10.1016/j.aquatox.2017.06.013>.
- Xie, H., Wang, X., Chen, J., Li, X., Jia, G., Zou, Y., Zhang, Y., Cui, Y., 2019. Occurrence, distribution and ecological risks of antibiotics and pesticides in coastal waters around Liaodong Peninsula, China. *Sci. Total Environ.* 656, 946–951. <https://doi.org/10.1016/j.scitotenv.2018.11.449>.
- Yin, J., Hong, X., Ma, L., Liu, R., Bu, Y., 2020. Non-targeted metabolomic profiling of atrazine in *Caenorhabditis elegans* using UHPLC-QE Orbitrap/MS. *Ecotoxicol. Environ. Saf.* 206, 111170. <https://doi.org/10.1016/j.ecoenv.2020.111170>.
- Yu, J., Bian, Z., Tian, X., Zhang, J., Zhang, R., Zheng, H., 2018. Atrazine and its metabolites in surface and well waters in rural area and its human and ecotoxicological risk assessment of Henan province, China. *Hum. Ecol. Risk Assess.* 24 (1), 1–13. <https://doi.org/10.1080/10807039.2017.1311768>.