Assessment of atrazine contamination in the Sele River estuary: spatial distribution, human health risks, and ecological implications in Southern Europe

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Abstract

Background Overuse of pesticides is a major worldwide problem for the environment and human health. Atrazine (ATR) is a synthetic triazine herbicide that is typically used to manage crops and although it was banned many years ago, it was detected frequently with a high persistence in the aquatic environments. This study assesses the human and environment health risks, temporal patterns and spatial distribution of ATR and its degradation products (DPs) in the Sele River estuary within the Southern European context.. It specifically investigates their occurrence in the water dissolved phase (WDP), suspended particulate matter (SPM), and sediment.

Results Sampling was conducted across 10 sites throughout the year's four seasons. Amounts of ATR and its DPs detected ranged from 20.1 to 96.5 ng L^{-1} in WDP, from 5.4 to 60.2 ng L^{-1} in SPM, and from 4.7 to 19.8 ng g^{-1} in sediment samples, signifying some pollution levels. Spatial distribution mechanisms revealed a southward movement of ATR and its DPs pollution from the Sele River mouth, intensifying during the rainy season. In this study area, a risk evaluation was also carried out. No sample contained ATR or its DPs in concentrations above the recommended limits, which pose a Non-carcinogenic and Carcinogenic risk. The environmental risk was low. Additionally, the determined Incremental lifetime cancer risk (ILCR) value was within the allowable range.

Conclusion Despite its long-standing prohibition, this study investigate ATR levels in the water and sediments of Sele River in Southern Europe. Beyond simply delineating the pollution status of Sele River, this research delineates its ecological repercussions on the Thyrrenian Sea, providing essential data for norms and laws related to water contamination.

Keywords Monitorings, Pollutants, Degradation products, Non carcinogenic and carcinogenic risk, Environmental risk
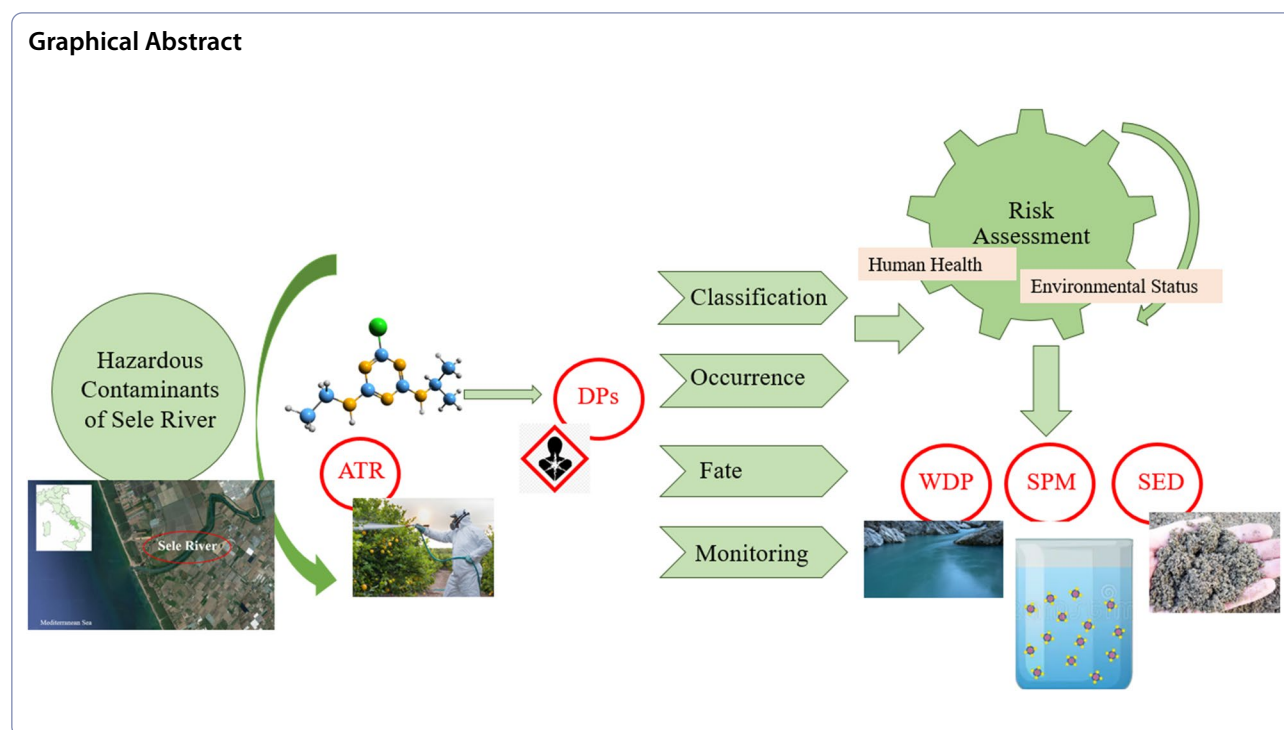
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Graphical Abstract

Background

Aquatic ecosystem safety is mainly centred on how common organic contaminants are transformed in aquatic environments, which is more complicated than their destiny in surface water or soil.. The use of pesticides to safeguard food production and satisfy global demand is common, but they are also ubiquitous environmental pollutants that have a negative impact on human health, biodiversity, and water quality [1, 2]. Pesticides pose a concern because of their physic-chemical properties and resilience, but most importantly because they may metabolize and produce new degradation products (DPs) [3, 4].

DPs can originate from different degradation mechanisms of pesticides. These degradation actions in the environment comprises two main processes: biological degradation and chemical degradation. Chemical degradation, in turn, is further categorized into hydrolysis and photolysis. Both hydrolysis and photolysis play significant roles in the breakdown of pesticides within the environment.

Hydrolysis involves the chemical breakdown of pesticide molecules through reactions targeting specific chemical structures within them, such as ester bonds, ether bonds, and amide bonds [5]. Photolysis, on the other hand, involves the degradation of pesticides through exposure to light radiation, wherein the energy from light breaks molecular bonds within the compound, initiating internal reactions. Many pesticides exhibit a high sensitivity to photolysis due to their inherent structural properties [6]. Biological degradation, conversely, is facilitated by microorganisms that catalyze various reactions including hydrolysis, oxidation, alkylation, and dealkylation. Biodegradation can be understood as the conversion of complex pesticide substances into simpler compounds through microbial activity [7, 8].

The produced DPs are often at least as hazardous as the parent chemicals, and because of their extremely polar and hydrophilic properties, they may easily pass into aquatic ecosystems [9–11]. (ATR and its DPs have been under intensive scientific review for over a decade due to its negative effects on growth, reproduction, development and other physiological functions in aquatic organisms [12]. Mercurio et al. has revealed the potentially high toxicity of ATR degradation substances to nonphototrophic organisms [13].

According to the literature, ATR's pollution resulted in hazardous effects on fish such as immunosuppression, oxidative stress, inflammation, and high acceptability to infection [14, 15]. These substances pose a major threat to human health since they may result in the development of conditions that affect the immunological, respiratory, reproductive, neurological, gastrointestinal, and endocrine systems as well as the skin and the genital tract [16, 17].

Mostly used as a specific herbicide, ATR stops photosynthesis in broadleaf weeds. Mostly applied as a specific herbicide, ATR finds extensive application in corn

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and sugar cane cultivation, owing to its notable efficacy in weed control [18] Consequently, its widespread adoption on a global scale has ensued. Nonetheless, owing to its considerable propensity for environmental contamination, the European Union instituted an absolute ban on ATR employment in 2004 [19]. Despite this regulatory measure, ATR continues to be extensively utilized in other regions, including the United States, Brazil, India, and China. Because this pesticide is very polar and hydrophilic (Kow=2.61), it may easily seep out of the ground and be transported by rural streams through runoff, which then enters estuarine ecosystems. [20].

The degradation process develops during the transit of herbicides via leaching from soil into adjacent surface marine water, and it is dependent on the marine environment, atmospheric conditions and the characteristics of the herbicide. ATR in water and in soil is a very persistent chemical. [21]. Aquatic organisms may be at risk due to ATR, the herbicide that is most commonly identified in estuarine environments and has a 100% detection frequency has been found everywhere [22]. The half-life of ATR can range from numerous weeks to approximately 2 years across various environmental contexts, primarily due to its non-biodegradable characteristics and its resilience against microbiological degradation in aquatic ecosystems [23, 24]. Its main degradation products defined as primary are desethylatrazine (DEA), desisopropylatrazine (DIA), and hydroxyatrazine (HA), while desethylhydroxyatrazine (DEHA) and desisopropylhydroxyatrazine (DIHA) are defined as secondary degradation products and derive mainly from chemical and biological degradation processes (Fig. 1). Because of their comparable or greater ecotoxicity to the ATR parent, the alkyl-substituted derivatives, DEA and DIA, represent important degradation products that have been researched. The hydroxyl-substituted product, HA, appears to be the principal product of chemical degradation and constitutes up the majority in aquatic environments [25]. In terms of toxicity, ATR is a compound that, with prolonged or repeated exposure, may result in organ damage, skin sensitization, and allergic skin responses. Moreover ATR acts also as an endocrine disruptor, the capacity of this herbicide to interfere with the vertebrate endocrine system is broadly recognized, but the mechanisms and responses usually differ among species [26]. It is categorized as possibly carcinogenic to humans in Group III and has the potential to negatively impact human health [27, 28]. In Europe, ATR was prohibited in 2004, however, considering that several countries surface waterways still contain this herbicide, the Directive 2013/39/EU [29] determines 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. Nevertheless, notwithstanding the prohibition, ATR and its metabolites have recurrently been detected in significant concentrations, surpassing water quality standards, in several European countries such as Spain, Slovenia, Hungary, Portugal, and Germany over the past decade [30]. Furthermore, recent studies documented the presence of ATR and its DPs in water of Italy [28, 31].

The vertical and horizontal distributions of ATR in water, suspended particles, and sediment may provide significant knowledge about the dynamics of herbicide consumption in marine environments because of its extensive application. The ATR transmission mechanism from terrestrial watershed to marine environment is dependent on variations in salinity, DOC, seawater depth, and temperature on a regional and temporal scale [32]. This research evaluates the amounts of ATR and its DPs found from the Sele River, one of the important rivers of the Campania plain. Situated in a rich region of southern Italy, the Campania plain has sustained the development of agriculture and farming during history. Rich farming techniques, such raising cattle on buffalo farms and producing fruits and vegetables on a huge scale, are common in this area, in particular the Plane of Sele River is an area characterized by an intensive agriculture and greenhouse cultures [33, 34]. Currently, there is a significant lack of research examining the health risks associated with atrazine and its degradation products. Therefore, given the scarcity of data regarding regional ATR contamination and its DPs in water and sediment in Italy, the main objective of the study was to assess the concentrations of atrazine (ATR) and its degradation products (DPs) in the Sele River, as well as the potential risks to human health resulting from exposure to them. In detail, the research aimed to (i) estimate the concentrations of ATR and its DPs in WDP, SPM and sediment phases; (ii) evaluate their distribution between water and sediment; (iii) analyze the spatial and temporal variations in the Sele River; (iv) Assess the potential non-carcinogenic and carcinogenic risks to human health...

Materials and methods
Area of study
The Sele plain, of about 500 km^2, constitutes a very fertile region of Campania Region, divided into right and left areas based to the Sele River's flow. This region is bordered to the north by the Meridional chains of Mt Picentini, to the east by the hills of the medium Sele, to the south by the chains of the sub-Lucan Appennines, and to the west by the Tyrrhenian Sea of the Gulf of Salerno. From a geological perspective, the Sele Plain is an area that was just recently developed. This is because the Sele River, in particular, was responsible for accumulating alluvial debris from the adjacent mounts and generating
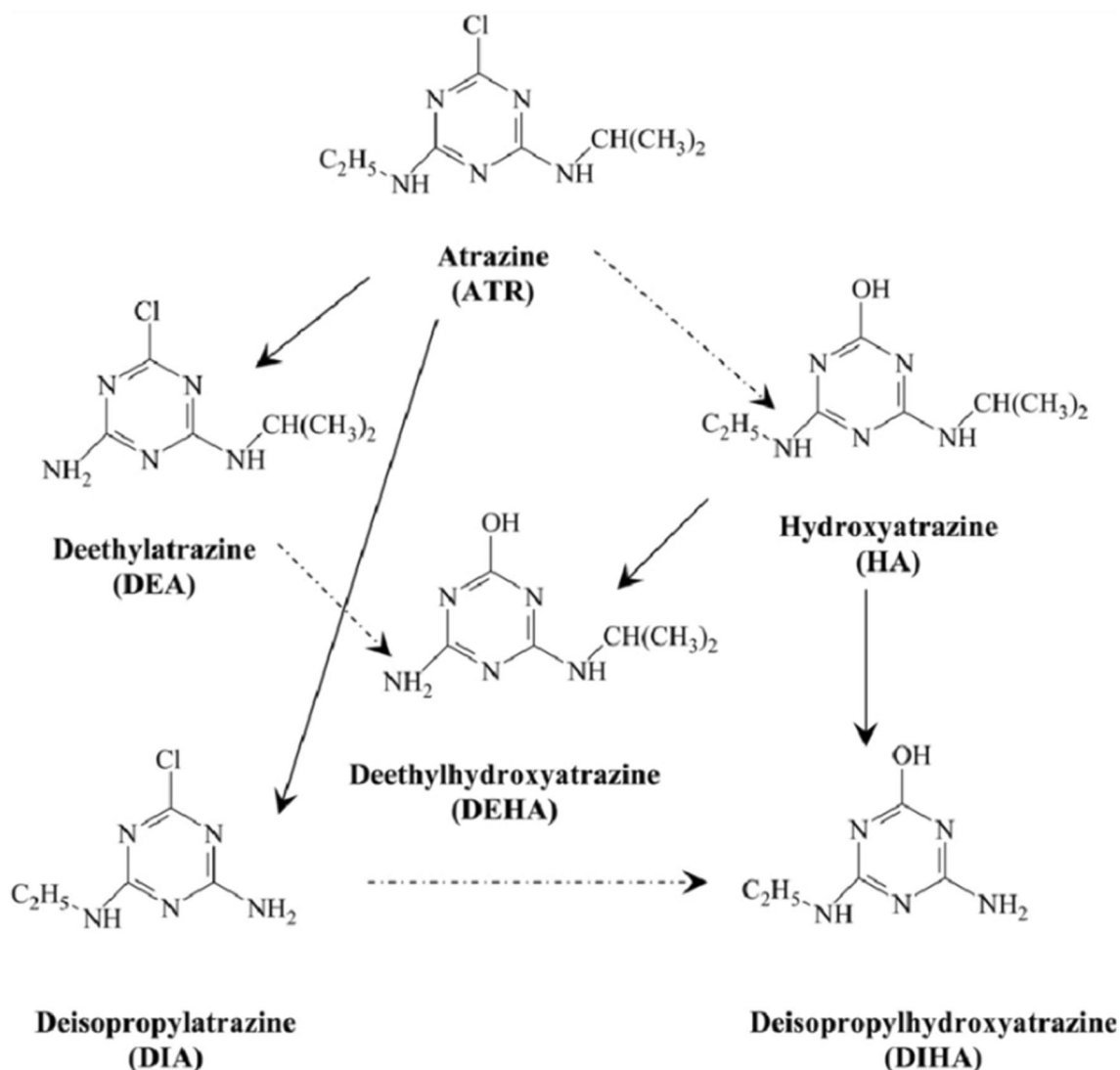
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Fig. 1 Degradation pathways of atrazine to primary and secondary metabolites [70, 71]

deep and fertile soils. Due to these characteristics, the Sele Plain is the Salerno province's most significant and productive lung. In this study area the climate is usually Mediterranean with wet and moderate winter and dry summer, rainfall is concentrated from autumn to spring and the principal crops are potatoes, vegetables, peach, apricots and pears [35, 36] (Fig. 2).

Sampling

The sampling procedure has been previously described by De Rosa et al. [34]. Briefly, between 2020 and 2021, water and sediment samples were gathered in the Sele River to evaluate the spatio-temporal distribution of different classes of pollutants including ATR and its DPs. The water samples were collected in triplicate, and Fig. 2 shows the sampling points stations. At a depth of about 20 cm in the river, surface water samples were taken with pre-cleaned 2.5 L glass bottles, transferred to the laboratory and stored at 4 °C until analysis The samples were filtered via glass fiber filter (47 mm 0.7 m; Whatman, Maidstone, UK) to distinct the suspended particle matter (SPM) and water dissolved phase (WDP) fractions. In the spring season (April 2021), at the 10 sampling locations, sediment (SED) samples (0–5 cm) were taken 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 [37, 38].
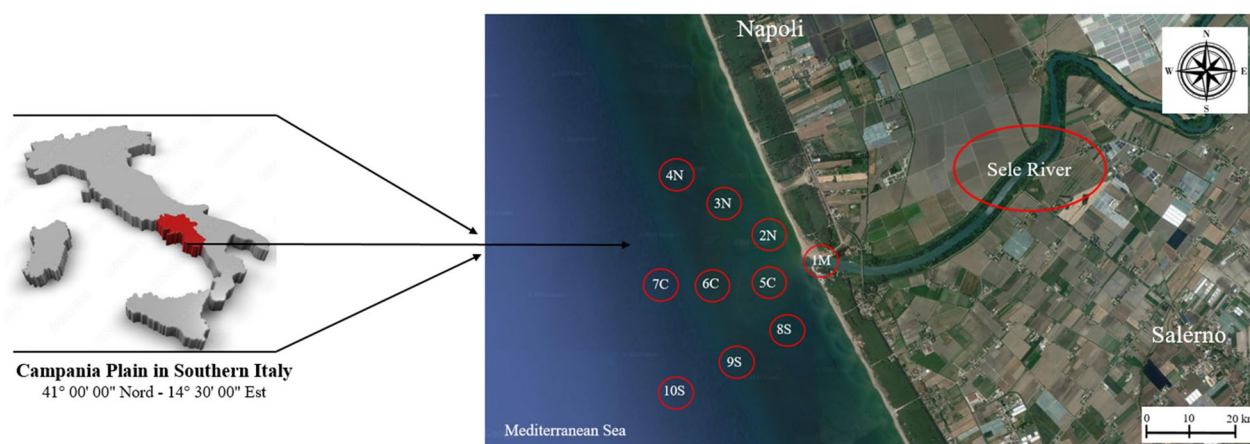
Fig. 2 Map of study area and location of sampling sites in Campania Plain, southern Italy

Instrumental analysis of ATR and DPs

Instrumental analysis for the determination of ATR and its DPs has previously been discussed in detail by Triassi et al. [28]. A Thermo Scientific™ UltiMate™ 3000UHPLC coupled to a TSQ Fortis Triple Quadrupole was used. The separation of analytes was accomplished using a reversed-phase Acclaim C18 column (4 μm particle size, 250×4.6 mm). The mobile phase consisted of LC–MS grade water/methanol (95:5) as eluent A and LC–MS grade methanol/water (95:5) as eluent B, both containing 0.1% formic acid/5 mM ammonium formate. The column temperature was maintained at +25 °C, with a flow rate of 300 μL min-1 and an injection volume of 2 μL. Gradient elution was conducted by altering the proportion of solvent A to solvent B as follows: 0 min at 2.0% B, 1 min at 2% B, 2 min at 50% B, 9 min at 98% B, 12 min at 98% B, and 12.1 min back to 2% B.

Method selectivity was ensured by monitoring two transitions per compound at the analyte's retention time, corresponding to the transition between the precursor ion and the two most abundant product ions. MS Quantification (SRM1) utilized the most abundant ion, while confirmation (SRM2) used the other. Detailed LC and MS conditions are provided in Table S1, and SRM details are summarized in Table S2.

Extraction samples method

The ATR and its degradation products were determined using the multi-residue method outlined by Climent et al. [39]. Specifically, 500 mL of water samples were filtered through 0.45 μm glass fiber filters, and the resulting filtrates were preconcentrated using a peristaltic pump at a consistent flow rate of 7 mL min^{-1} through SPE Oasis HLB cartridges. Prior to use, these cartridges were preconditioned with 5 mL of acetone, 5 mL of acetonitrile,

and 10 mL of Milli-Q water.After the loading phase, the cartridges underwent a 5-min air-drying period, then underwent elution with 4 mL of acetone followed by 4 mL of acetonitrile. Afterwards, the samples were dried using a nitrogen stream and reconstituted in 100 μL of methanol/water (1:1) for LC–MS/MS analysis. Considering the extraction method, the extracts were preconcentrated with a 1:5000 factor. ATR and DPs adhered to particulate matter (SPM), retained by glass fiber filters (47 mm×0.7 μm; Whatman, Maidstone, UK), and extracted through sonication for 15 min. Later on, the extracts were dried using a nitrogen stream and reconstituted in 100 μL of methanol/water (1:1) for LC–MS/MS analysis. In this case as well considering the extraction method, the extracts were preconcentrated with a 1:5000 factor [23].

For sediment samples (5.0 g), a processing step involved using 10 mL of methanol/acetone (1:1), followed by centrifugation. The dried extract was then reconstituted in 500 μL of methanol/water (1:1) for subsequent analysis via LC–MS/MS [40].

Quality control and quality assurance

The method validation was conducted to assess data quality by determining precision, accuracy, linearity, limits of detection (LODs), limits of quantification (LOQs), and uncertainty. The analytical parameters were evaluated using samples of ultrapure water UPLC grade and uncontaminated natural water spiked with predetermined concentrations of the studied compounds. The matrix effect was assessed in duplicate by comparing the analyte signal obtained from pre-concentrating 500 mL of ultrapure water UPLC grade with that obtained from preconcentrating 500 mL of river water, each spiked with a concentration of 0.00125 ng L^{-1} of all compounds. The

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quantification of the samples was carried out through external calibration using matrix-matched standards to correct signal enhancement or suppression. The linearity of the calibration curves for water and SPM phases was assessed across an instrumental concentration range of 6.25–1000.00 ng/L, corresponding to a concentration range of 0.00125 to 0.2 ng/L, using calibration standards prepared in uncontaminated river water (matrix-matched calibration standards) to ensure accurate quantification. For sediment, the range of the calibration curve was between 0.0292 and 10.00 μg L^{-1}, corresponding to a concentration range of 0.00292–1.00 ng g^{-1}.

Terbuthylazine was introduced into samples as the surrogate standard for LC–MS/MS analysis, at the concentration of 50 ng L^{-1}, before extraction to validate the analytical process. Due to the widespread presence of terbuthylazine as a contaminant [41], the recovery process involved assessing the matrix effect by comparing the analyte signal obtained from concentrating 500 mL of ultrapure water (UPLC grade) with the signal obtained from both non-spiked and spiked matrices.

In batches of 10 samples, certified reference materials were analyzed alongside samples using identical extraction techniques to identify potential interfering chemicals. Limit of Detection (LODs) and Limit of quantification (LOQs) were calculated as 3 and 10 times the signal-to-noise ratio for each analyte. Specifically, for WDP and SPM, the effective LODs and LOQs, determined considering the concentration factor (1:5000) ranged from 0.000375 to 0.000615 ng L^{-1} and 0.00125 to 0.00205 ng L^{-1}, respectively. In sediment samples, the amounts varied from 0.000875 to 0.00121 ng g^{-1} and 0.00292 to 0.00403 ng g^{-1}, respectively.

Surrogate averaged recovery rates were 89.6±5.5% in WDP, 90.5±7.0% in SPM, and 93.2±3.0% in sediment samples. These surrogate recoveries were considered in the calculation of ATR and DP results.

Health risk estimation

River systems are important components of environment, exhibiting complex hydrodynamics and rich biodiversity. Moreover, with pollution development and population growth in river systems, large amounts of pollutants, including ATR and DPs, are typically discharged into estuaries. In this study health risk assessment was evaluated and categorized into two classes: carcinogenic and non-carcinogenic risk.

It was estimated that the direct ingestion and dermal absorption of ATR via contact to water by adhering to the exposed skin are the most frequent way of polluted water [42]. Humans are exposed to contaminants including pesticides in water and sediments through several pathways or routes. Notable among such pathways are direct or indirect ingestion of substrate particles and dermal absorption of trace elements in particles adhered to exposed skin; as the reference dose of inhalation and unit risk of atrazine inhalation were not available in the recommended methods, only the risks via accidental ingestion and dermal contact exposure routes were assessed.

Several study in litterature have estimated the potential risk to human health that could arise from the consumption of pesticide contaminated food (dietary intake). However, there is the need to estimate the risk to human health through non dietary exposures. These risks are predicted by some risk assessment models which include the chronic daily intake (CDI) and the incremental lifetime cancer risk (ILCR).

As shown in Table S3, the slope factors for carcinogenic pollutants and reference dosages for noncarcinogenic substances were obtained from databases including the Integrated Risk Information System (IRIS, US EPA). In the health risk evaluation, 1×10^{-6} was used as the acceptable critical threshold of lifetime cancer risk for individuals in accordance with the suggested tolerable risks gave by the US EPA [43].

Equations (1) and (2) were used to estimate the exposure pathways through eating and cutaneous absorption. Equations (3) and (4) were used to determine the atrazine's and its DPs non-carcinogenic health risk and incremental lifetime cancer risk, respectively.

$$\mathrm{CDI_{Ingestion}} = (C * IR * EF * ED)/(BW * AT) \quad (1)$$

$$\mathrm{CDI_{Dermal}} = (C * SA * Kp * ABF * ET * EF * ED * CF)/(BW * AT) \quad (2)$$

$$\mathrm{HQ} = \sum CDI/RFD \quad (3)$$

$$\mathrm{ILCR} = \sum CDI * SF \quad (4)$$

so CDI is chronic daily intake (mg/kg*d); C indicates the amount of the target contaminants(mg/L); IR is the intake rate (L/d); EF suggest the exposure frequency (d/y) that was 30 and 70 years for non-cancer and cancer risk, respectively, ED is the exposure period (years); BW is the body weight (kg); AT is the standard exposure time (days); SA is the skin exposure area (cm^2); Kp is the permeability coefficient (cm/h); ABF is the dermal absorption factor and ET is the Exposure time (h/d). RfD value for ingestion is RfDo and for dermal contact with contaminated water and sediment is RfD-ABS (RfDo×ABS$_{GI}$). ABS$_{GI}$ is considered as the fraction absorbed in the gastrointestinal tract in the main toxicity study. For the calculation of ILCR, SF$_O$ (mg/kg/day) and SF$_O$×ABS$_{GI}$ represent the slop factor of direct ingestion

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and dermal contact, respectively.Parameters used for exposure analysis of ATR and its DPs via ingestion and dermal pathways are reported in Table S3 in Supplementary Material Section [44].

Environmental risk assessment

The environmental risk assessment was conducted for this study. The potential ecological risks associated with the residues of ATR, HA, DEA and DIA identified in the analysed fractions and were evaluated. The presence of these pollutants in freshwater and marine ecosystems can cause significant harm and pose a serious threat to aquatic organisms. According to Barbieri et al. [45] the hazard quotient (HQ) approach was calculated using the ratio of the mean or maximum measured environmental concentration (MEC) to the predicted no-effect concentration (PNEC), as shown by the Eq. (5):

$$HQ = \frac{MEC}{PNEC} \tag{5}$$

PNEC values were procured from the NORMAN Ecotoxicology Database (https://www.norman-network.com/nds/ecotox/) [45].

In this study, the mean concentration and the maximum concentration measured for each pesticide were used as MEC to assess the general-case scenario (HQmean) and to evaluate the worst-case scenario (HQmax), respectively. In addition, the HQ of the ATR, HA, DEA and DIA mixture (HQmix) was evaluated as the sum of individual HQm values of each contaminant.

High MEC and/or low PNEC are indicators of an important environmental risk. To best reflect freshwater, marine water systems, native aquatic organisms from trophic levels of fish and aquatic invertebrates, were considered in this study.

Three risk levels were identified based on the value of HQ: HQ values below 1 indicate zero or low risk, while HQ values between 1 and 10 anticipate moderate risk, and HQ values above 10 suggest high environmental risk.

Results and discussions

Levels of atrazine and its DPs

The extensive and occasionally insufficient application of herbicides has led to the development of resistance to these chemical agents. Consequently, there is an ongoing necessity for the development and utilisation of new herbicides [46], which may possess increased toxicity. According to Heap [47], there have been reports of 1066 cases across 70 countries detailing instances of weed resistance to herbicides, thereby presenting a significant public health concern.

Due to the implications for human health and the environment, regulations and legislation in numerous countries, particularly those with well-established water quality laws, impose restrictions on the usage of herbicides. Climent et al. [39] highlight that within the European Union, the legislation governing the maximum permissible concentrations of pesticides in drinking water stands as the most rigorous globally.This study analyzed the levels of ATR and DPs in the Sele River area, the amounts of these contaminants in water, SPM and sediment in the Sele River study area were reported in Tables 1, 2 and 3. The total concentrations of ATR and DPs in WDP ranged from 20.1 to 96.5 ng/L^{-1} with mean value of 54.1. These results revealed that WDP had the greatest concentrations in the Sele River [20, 48]. In particular average concentrations obtained indicate higher concentrations for HA (30.8 ng L^{-1}) followed by DIA (6.34 ng L^{-1}), DEHA (6.27 ng L^{-1}), DIHA (5.12 ng L^{-1}), ATR (3.18 ng L^{-1}) and DEA (2.28 ng L^{-1}) The diverse structural and chemical characteristics of ATR degradation products affect their variable interfacial partitioning. ATR, DIA, and DEA are significantly polar substances, hence their greater amounts in the WDP can be explained by their chemical-physical properties [49], in fact because ATR has approximately symmetric molecular structure, the substance has strong hydrophobicity and therefore low solubility, making ATR persistent in aqueous solution. On the other hand, the hydrolysis processes that take place in water might justify the presence of HA, DIHA, and DEHA. The environmental behaviour of ATR depends upon several factors, including retention, transformation and transport processes, as well as by the interaction between them [50], in fact both in water and in sediments, ATR is subjected to numerous chemical reactions such as dechlorination, dealkylation of amino groups and hydroxylation [48]. The concentration of ATR could also be due to its properties, in fact it has a water solubility of 33 mg L^{-1} (20 °C), a melting point of 175.8 °C, and is readily soluble in organic solvents [51]. According to Urseler et al. ATR has a half-life of 100 days in water and 32–128 days in soil, making it a very persistent chemical [52].

For SPM, concentrations ranged from 5.4 to 60.2 ng L^{-1}, with a mean value of 27.1 ng L^{-1} (equivalent to 129.9 ng g^{-1}). The average sample concentrations obtained indicate higher concentrations for HA (15.5 ng L^{-1}) followed by DIA (3.63 ng L^{-1}), DEHA (3.18 ng L^{-1}), DIHA (2.40 ng L^{-1}), ATR (1.65 ng L^{-1}) and DEA (0.75 ng L^{-1}).

Comparisons between the findings of this study and other studies that have assessed the existence of ATR and its DPs in both WDP and SPM samples are currently limited with those in the literature. Particularly, upon comparing the data acquired with the outcomes of the previous investigation by Triassi et al. [28], it

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Table 1 Overview of the sampling area and mean concentrations (±standard deviations $n=3$) of ATR and its metabolites in the water dissolved phase (WDP) of the Sele River, southern Italy

Sampling area

Site number identification	Site characteristics	Site location	Campaigns	Compound in WDP ng L^{-1}						
				ATR	DIHA	DEHA	DIA	DEA	HA	Sum ATR and its DPs
1 (River water)	Sele River mouth	40° 28′ 55″ N 14° 56′ 33″ E	November	7.20±0.10	8.77±0.11	7.71±0.14	8.89±0.10	5.16±0.17	40.21±0.52	77.94±0.50
			February	6.22±0.15	9.01±0.10	10.08±0.16	11.02±0.47	6.34±0.07	52.68±0.80	96.56±1.04
			April	5.47±0.10	6.84±0.31	8.34±0.10	9.74±0.11	3.62±0.10	39.45±0.33	73.46±0.28
			July	3.21±0.13	5.74±0.07	6.78±0.13	7.05±0.12	2.32±0.15	23.74±0.21	48.84±0.65
2 (Sea water)	River mouth 500 m north	40° 29′ 04″ N 14° 56′ 14″ E	November	4.54±0.07	5.32±0.14	6.76±0.37	7.12±0.10	1.22±0.24	25.44±0.77	50.40±0.42
			February	3.96±0.14	7.12±0.10	8.14±0.17	7.08±0.35	4.02±0.25	42.88±0.23	73.20±0.55
			April	2.41±0.10	4.16±0.67	5.02±0.52	4.60±0.17	3.02±0.50	20.65±0.11	39.86±1.10
			July	1.52±0.07	3.14±0.10	3.89±0.28	4.01±0.10	0.92±0.27	18.20±0.21	31.68±0.38
3 (Sea water)	River mouth 1000 m north	40° 29′ 12″ N 14° 55′ 56″ E	November	1.00±0.09	5.87±0.29	5.13±0.39	7.32±0.14	1.17±0.30	20.39±0.14	40.88±1.00
			February	2.26±0.32	6.01±0.17	7.06±0.13	6.97±0.21	2.82±0.22	39.45±0.40	64.57±0.32
			April	1.03±0.07	2.41±0.08	5.07±0.15	4.04±0.31	1.01±0.21	20.12±0.44	33.68±0.71
			July	0.61±0.14	1.98±0.14	4.13±0.16	5.54±0.08	1.76±0.11	18.12±0.18	32.14±0.63
4 (Sea water)	River mouth 1500 m north	40° 29′ 20″ N 14° 55′ 38″ E	November	1.44±0.12	3.41±0.24	4.42±0.48	6.82±0.48	0.94±0.22	20.46±0.09	37.49±0.71
			February	2.96±0.08	6.14±0.20	8.47±0.26	6.36±0.18	2.98±0.10	42.12±0.01	69.03±0.52
			April	1.10±0.11	3.17±0.60	3.52±0.12	4.26±0.09	0.91±0.55	16.14±0.29	29.10±1.25
			July	0.17±0.05	2.16±0.12	2.15±0.19	2.31±0.14	1.23±0.69	12.07±0.10	20.09±0.10
5 (Sea water)	River mouth 500 m west	40° 28′ 55″ N 14° 56′ 12″ E	November	4.02±0.09	8.78±0.21	9.01±0.13	7.93±0.41	4.01±0.23	28.27±0.15	62.02±0.51
			February	5.55±0.06	6.01±0.12	7.12±0.09	6.85±0.87	1.05±0.05	60.30±0.40	86.88±1.20
			April	2.98±0.11	3.01±0.10	5.98±0.09	5.98±0.10	1.88±0.48	33.80±0.12	53.63±0.81
			July	2.01±0.09	3.65±0.40	5.10±0.25	6.32±0.20	2.10±0.11	20.45±0.22	39.63±0.49
6 (Sea water)	River mouth 1000 m west	40° 28′ 55″ N 14° 55′ 50″ E	November	3.92±0.17	6.21±0.61	5.41±0.10	8.48±0.09	1.42±0.37	20.55±0.24	45.99±0.63
			February	4.92±0.08	8.10±0.33	8.70±0.15	6.34±0.18	1.16±0.19	52.99±0.62	82.21±0.49
			April	2.93±0.09	4.15±0.21	6.13±0.25	4.01±0.19	1.42±0.10	31.55±0.13	50.19±0.33
			July	2.25±0.09	3.45±0.14	3.99±0.27	5.17±0.26	0.77±0.30	18.70±0.85	34.33±0.90
7 (Sea water)	River mouth 1500 m west	40° 28′ 55″ N 14° 55′ 28″ E	November	3.45±0.10	5.16±0.13	3.60±0.70	6.91±0.61	1.01±0.16	21.25±0.07	41.38±1.21
			February	5.12±0.09	6.04±0.11	10.00±0.17	5.55±0.60	2.23±0.22	50.80±0.77	79.74±0.87
			April	3.12±0.14	2.61±0.10	4.48±0.15	2.93±0.15	0.99±0.41	28.45±0.70	42.58±0.71
			July	1.87±0.13	1.15±0.26	3.10±0.10	3.20±0.57	1.21±0.10	14.25±0.15	24.78±1.00
8 (Sea water)	River mouth 500 m south	40° 28′ 47″ N 14° 56′ 16″ E	November	4.98±0.18	7.07±0.26	8.10±0.51	9.19±0.11	2.91±0.36	35.56±0.31	67.81±0.85
			February	5.78±0.10	9.86±0.10	10.98±0.10	8.32±0.39	6.12±0.10	55.50±0.11	93.35±0.94
			April	4.12±0.25	3.19±0.17	6.01±0.09	7.99±0.21	3.10±0.19	30.55±0.26	54.96±0.49
			July	2.88±0.20	4.21±0.21	5.12±0.42	5.74±0.48	3.47±0.21	22.96±0.36	44.38±1.48

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Table 1 (continued)

Sampling area

Site number identification	Site characteristics	Site location	Campaigns	Compound in WDP ng L⁻¹						
				ATR	DIHA	DEHA	DIA	DEA	HA	Sum ATR and its DPs
9 (Sea water)	River mouth 1000 m south	40° 28′ 39″ N 14° 55′ 56″ E	November	3.45±0.28	5.55±0.55	8.66±0.47	7.03±0.21	1.55±0.19	24.48±0.17	50.72±0.99
			February	4.12±0.12	6.98±0.13	9.45±0.45	7.49±0.10	2.98±0.21	50.72±0.30	81.74±0.38
			April	3.28±0.10	4.02±0.20	4.91±0.18	5.25±0.24	1.05±0.17	33.02±0.25	51.53±0.45
			July	2.10±0.32	4.56±0.07	3.78±0.31	6.01±0.18	3.89±0.22	20.63±0.32	40.97±0.68
10 (Sea water)	River mouth 1500 m south	40° 28′ 30″ N 14° 55′ 38″ E	November	2.87±0.20	6.31±0.31	7.15±0.35	7.55±0.10	1.11±0.31	25.98±0.40	50.97±1.05
			February	3.01±0.18	8.36±0.11	10.36±0.61	8.16±0.11	2.15±0.05	50.25±0.20	82.29±0.61
			April	2.26±0.10	3.15±0.24	3.98±0.12	3.98±0.22	1.01±0.20	31.05±0.21	45.43±0.55
			July	1.07±0.09	2.14±0.10	2.87±0.27	4.04±0.33	3.00±0.10	18.84±0.88	31.96±0.69

The samples were collected in triplicate

can be inferred that the values identified for the SPM phase in the analyzed rivers (Volturno River and Sele River) are comparable. To elaborate, the total amount detected ranged from 4.5 to 63.2 ng L⁻¹ with an average of 28.4 ng L⁻¹ for the Volturno River, and from 5.43 to 60.23 ng L⁻¹ (with a mean value of 27.15 ng L⁻¹) for the Sele River. Conversely, in the dissolved phase, the results of this study unveiled quantities ranging from 20.09 to 96.56 ng L⁻¹ (with a mean value of 54.0 ng L⁻¹). Furthermore, for this matrix as well, the findings exhibit consistency with those derived in the previous study, wherein the total amounts of ATR and DPs detected in WPD ranged from 18.1 to 105.5 ng L⁻¹, with a mean value of 54.4 ng L⁻¹ Instead, Climent et al. [39] in a 2019 study reports data obtained from a study on the most used pesticides in Chile and in relation to the concentrations of DIHA and HA found, the highest values were found in the SPM with maximum of 1123 µg/kg (1123 ng/g⁻¹) and 1195 µg/kg (1195 ng/g⁻¹), respectively [39]. Higher values were also found by Peng et al. [53] that identified a maximum concentration of 1726 ng L⁻¹ of ATR in China, in the Yangtze River Delta, while Battaglin et al. [54] in 86 water samples (183 ng L⁻¹) finds ATR as one of the most frequently detected compounds.

In stagnate surface waters, ATR can remain floating or it may be absorbed by the sediment. Adsorption can occur in this phase following the diffusion of herbicides into sedimentary pore fluids or following a sediment disturbance event, such as cleaning or waves. Sediment resuspension could occur when rapid water flows into the body of water following periods of intense rainfall. ATR or its DPs may be removed from water during such disturbance episodes by attached to sediment and sinking to the bottom of the water body. In addition, ATR can disperse while it is still in the water above it or after it has attached itself to sediments through biotic and abiotic processes. This is possible by dechlorination, which is basically a chemical hydrolysis process, or by *N*-dealkylation and ring destruction mediated by microorganisms [55].

N-Dealkylation of ATR develops DEA and DIA whereas HA is the first hydrolytic product. The dealkylated metabolites are further degraded to hydroxylated atrazine products such as DEHA and DIHA. Furthermore, DEA and DIA are less adsorbed onto sand, most likely as a result of their greater mobility and lower sorption than ATR [56].

For the sediment samples the results are detailed in Table 3. The average concentrations obtained indicate higher levels for HA (3.58 ng g⁻¹), followed by ATR (3.29 ng g⁻¹), DEA (1.91 ng g g⁻¹), DEHA (1.86 ng g⁻¹), DIA (0.89 ng g g⁻¹), and DIHA (0.74 ng g g⁻¹). Nevertheless, for the Volturno River, the

Table 2 Overview of the sampling area and mean concentrations (±standard deviations $n=3$) of ATR and its metabolites in the suspended particulate matter (SPM) of the Sele River, southern Italy

Sampling location				Compound in SPM ng L⁻¹ (ng g⁻¹)						
Site number identification	Site characteristics	Site location	Campaigns	ATR	DIHA	DEHA	DIA	DEA	HA	Sum ATR and its DPs
1 (River water)	Sele River mouth	41° 01′ 19″ N 13° 55′ 26″ E	November	2.50±0.21 (25.10±1.60)	1.10±0.25 (11.81±1.50)	5.24±0.20 (39.62±2.00)	3.97±0.20 (31.07±1.89)	1.25±0.21 (7.43±1.80)	27.26±0.21 (241.27±1.41)	41.32±0.31 (356.3±4.12)
			February	4.02±0.15 (41.28±0.99)	5.17±0.26 (47.10±1.60)	4.99±0.25 (41.10±2.32)	7.62±0.48 (75.06±3.74)	2.02±0.25 (18.14±1.53)	36.41±0.25 (322.10±2.10)	60.23±0.63 (544.78±4.10)
			April	3.60±0.21 (16.40±1.20)	2.56±0.37 (17.68±1.60)	4.40±0.35 (21.34±1.50)	3.75±0.23 (28.97±0.95)	1.35±0.28 (7.85±1.24)	17.29±0.31 (78.41±1.15)	32.95±1.25 (170.65±8.07)
			July	3.55±0.25 (39.91±2.20)	2.98±0.23 (40.74±2.00)	5.34±0.16 (70.92±2.45)	4.08±0.17 (50.94±2.29)	1.00±0.09 (15.36±1.41)	5.17±0.23 (89.12±3.49)	22.12±0.26 (306.99±3.24)
2 (Sea water)	River mouth 500 m north	41° 01′ 05″ N 13° 55′ 38″ E	November	1.89±0.26 (11.29±1.89)	0.47±0.02 (2.45±0.40)	3.01±0.18 (29.48±2.41)	1.47±0.20 (16.74±2.03)	1.00±0.12 (7.89±0.70)	20.68±0.20 (184.72±2.56)	28.52±0.29 (252.57±5.87)
			February	1.51±0.11 (17.47±1.27)	2.97±0.12 (30.40±1.12)	2.01±0.07 (19.72±0.44)	7.41±0.26 (61.27±1.50)	0.39±0.04 (3.97±0.36)	24.69±0.32 (287.22±3.01)	38.98±0.72 (420.05±6.48)
			April	1.09±0.10 (7.69±1.23)	2.64±0.29 (21.52±1.80)	3.49±0.33 (29.79±2.83)	3.24±0.31 (29.71±2.97)	0.54±0.22 (3.41±1.48)	11.48±0.35 (90.71±1.99)	22.48±1.08 (182.83±9.45)
			July	1.99±0.18 (20.28±1.09)	1.18±0.26 (11.41±1.99)	3.87±0.28 (39.14±2.47)	1.97±0.21 (20.95±1.74)	0.49±0.10 (4.65±1.04)	3.85±0.17 (40.84±2.49)	13.35±0.18 (137.27±1.52)
3 (Sea water)	River mouth 1000 m north	41° 00′ 51″ N 13° 55′ 48″ E	November	1.01±0.10 (6.32±0.92)	0.10±0.06 (1.15±0.10)	2.99±0.32 (21.47±1.00)	1.58±0.32 (10.09±2.16)	0.54±0.14 (3.71±0.94)	21.44±0.32 (129.44±2.01)	27.66±0.47 (172.18±3.45)
			February	0.69±0.05 (1.41±0.09)	3.10±0.10 (20.37±0.41)	1.74±0.10 (10.96±0.45)	6.03±0.10 (40.27±0.81)	0.10±0.02 (1.23±0.13)	20.38±0.16 (159.43±1.31)	32.04±0.14 (233.67±1.87)
			April	0.97±0.10 (6.88±1.89)	2.00±0.16 (25.15±0.99)	2.89±0.48 (20.85±2.87)	2.99±0.22 (32.66±2.40)	0.36±0.12 (3.09±1.23)	7.98±0.17 (81.27±1.70)	17.19±0.57 (169.9±3.41)
			July	1.10±0.12 (10.97±1.15)	0.68±0.10 (8.47±2.10)	2.15±0.20 (25.37±2.01)	1.03±0.13 (29.22±1.66)	0.09±0.01 (1.18±0.14)	2.78±0.41 (36.69±4.48)	7.83±1.41 (111.9±9.62)
4 (Sea water)	River mouth 1500 m north	41° 00′ 33″ N 13° 55′ 49″ E	November	0.78±0.19 (4.87±0.83)	0.11±0.05 (0.39±0.08)	2.85±0.26 (15.34±1.18)	0.87±0.10 (2.48±0.73)	0.45±0.17 (97.69±2.15)	17.48±0.32 (97.58±1.10)	22.54±0.28 (218.35±2.63)
			February	0.22±0.05 (0.64±0.03)	2.63±0.33 (7.98±1.15)	2.01±0.19 (6.10±0.52)	4.86±0.18 (17.54±0.62)	0.10±0.05 (0.47±0.15)	22.87±0.21 (70.68±0.91)	32.69±0.87 (103.41±2.54)
			April	0.49±0.16 (4.86±1.43)	1.60±0.32 (15.16±2.56)	1.57±0.38 (15.10±1.89)	2.84±0.28 (18.42±1.99)	0.26±0.05 (2.58±0.68)	7.12±0.32 (58.90±2.21)	13.88±1.10 (115.02±11.10)
			July	1.36±0.13 (11.57±1.25)	0.36±0.08 (2.74±0.70)	1.26±0.14 (12.53±0.86)	1.24±0.21 (10.10±1.09)	0.06±0.01 (0.29±0.04)	1.15±0.15 (12.10±1.41)	5.43±0.69 (49.33±6.00)

Table 2 (continued)

Sampling location				Compound in SPM ng ng L⁻¹ (ng g⁻¹)						
Site number identification	Site characteristics	Site location	Campaigns	ATR	DIHA	DEHA	DIA	DEA	HA	Sum ATR and its DPs
5 (Sea water)	River mouth 500 m west	41° 01′ 25″ N 13° 55′ 56″ E	November	2.41±0.20	1.38±0.12	3.97±0.22	2.71±0.22	1.16±0.14	21.18±0.33	32.81±0.72
				(19.41±1.62)	(12.20±1.18)	(40.12±1.99)	(21.24±1.29)	(7.50±1.11)	(178.25±2.80)	(278.72±7.12)
			February	1.47±0.17	6.31±0.18	2.10±0.20	7.93±0.20	1.28±0.12	29.72±0.24	48.81±0.68
				(11.39±0.64)	(38.8±1.35)	(19.21±1.48)	(60.48±1.52)	(10.09±0.93)	(234.18±1.82)	(374.15±4.25)
			April	2.10±0.28	2.97±0.22	3.62±0.32	3.97±0.32	0.96±0.10	10.81±0.22	24.43±0.71
				(13.10±2.64)	(19.33±2.01)	(25.26±1.81)	(37.99±2.29)	(6.32±1.10)	(89.51±1.67)	(191.51±4.86)
			July	1.98±0.21	1.26±0.29	3.74±0.19	3.41±0.28	0.59±0.18	5.90±0.10	16.88±0.63
				(12.90±1.14)	(15.79±2.10)	(23.64±1.45)	(20.36±1.34)	(3.87±0.81)	(35.52±1.21)	(112.08±5.32)
6 (Sea water)	River mouth 1000 m west	41° 01′ 00″ N 13° 54′ 52″ E	November	1.77±0.21	1.87±0.11	3.39±0.20	2.38±0.21	1.27±0.10	21.59±0.40	32.27±0.35
				(12.85±1.28)	(13.69±1.21)	(21.36±1.74)	(18.10±1.71)	(10.10±1.13)	(163.69±2.01)	(239.79±2.15)
			February	1.31±0.25	4.90±0.20	2.37±0.18	6.96±0.32	1.24±0.29	27.86±0.24	44.64±0.74
				(10.25±1.41)	(38.11±1.59)	(16.97±1.69)	(55.05±2.64)	(11.73±1.96)	(227.28±1.48)	(359.39±4.75)
			April	1.64±0.19	2.31±0.22	2.04±0.10	3.47±0.27	0.62±0.10	9.01±0.24	19.09±0.73
				(12.51±1.46)	(15.67±1.91)	(12.65±0.71)	(25.50±1.87)	(3.47±0.83)	(65.70±1.70)	(135.50±4.88)
			July	1.36±0.31	1.22±0.23	2.98±0.13	1.08±0.10	0.45±0.10	3.97±0.39	11.06±0.59
				(11.98±2.02)	(8.74±1.21)	(20.55±1.17)	(12.39±1.22)	(3.36±0.48)	(34.44±2.54)	(91.46±5.25)
7 (Sea water)	River mouth 1500 m west	41° 00′ 45″ N 13° 54′ 40″ E	November	0.61±0.10	1.89±0.11	3.24±0.16	1.84±0.15	1.00±0.12	11.48±0.20	20.06±0.11
				(5.79±1.26)	(17.57±0.85)	(29.51±1.47)	(17.44±1.52)	(9.10±1.09)	(109.54±2.10)	(188.95±2.12)
			February	1.10±0.10	2.83±0.14	1.78±0.14	4.55±0.26	1.21±0.16	15.28±0.30	26.75±0.68
				(8.72±1.20)	(29.77±1.20)	(13.94±1.09)	(49.22±2.06)	(8.97±1.28)	(129.14±2.40)	(239.76±6.26)
			April	1.10±0.16	1.71±0.10	1.98±0.18	2.84±0.28	0.45±0.05	7.08±0.28	15.16±0.69
				(7.64±1.18)	(13.02±1.16)	(15.30±1.41)	(20.95±2.13)	(3.46±0.41)	(65.47±2.16)	(125.84±4.10)
			July	1.01±0.12	1.14±0.17	2.90±0.31	1.21±0.15	0.38±0.09	2.52±0.30	9.16±0.77
				(9.16±1.10)	(11.26±1.64)	(26.32±2.71)	(11.96±1.47)	(3.80±0.90)	(26.97±2.94)	(89.47±5.10)

Table 2 (continued)

Sampling location				Compound in SPM ng L^{-1} (ng g^{-1})						
Site number identification	Site characteristics	Site location	Campaigns	ATR	DIHA	DEHA	DIA	DEA	HA	Sum ATR and its DPs
8 (Sea water)	River mouth 500 m south	41° 01′ 30″ N 13° 55′ 10″ E	November	2.99±0.10 (24.62±1.09)	2.25±0.26 (21.81±1.81)	4.95±0.23 (49.68±1.58)	3.29±0.29 (30.81±1.98)	1.99±0.19 (17.95±1.71)	22.75±0.26 (238.69±2.09)	38.22±0.33 (383.56±5.36)
			February	2.74±0.22 (26.07±1.72)	5.96±0.21 (57.39±1.99)	2.78±0.19 (25.75±1.98)	7.48±0.30 (6.00±2.06)	0.69±0.17 (6.52±1.58)	33.98±0.19 (322.17±1.84)	53.63±0.85 (443.9±6.65)
			April	1.38±0.10 (13.59±1.66)	2.49±0.27 (31.81±1.95)	4.02±0.33 (42.36±3.05)	4.69±0.22 (40.79±2.03)	0.98±0.16 (9.15±1.51)	15.30±0.47 (115.38±3.67)	28.86±1.15 (253.08±8.75)
			July	2.74±0.14 (31.69±1.12)	2.71±0.27 (24.51±2.10)	4.24±0.27 (41.97±2.65)	2.64±0.21 (31.69±1.56)	0.83±0.13 (8.14±1.26)	5.05±0.26 (55.28±3.25)	18.21±1.14 (193.28±12.16)
9 (Sea water)	River mouth 1000 m south	41° 01′ 47″ N 13° 55′ 05″ E	November	2.04±0.09 (13.91±0.63)	2.07±0.11 (14.12±0.73)	5.25±0.15 (35.76±1.02)	2.13±0.25 (14.53±1.72)	1.04±0.10 (7.11±0.66)	26.37±0.27 (179.49±1.84)	38.9±0.17 (264.92±0.89)
			February	2.61±0.23 (23.46±2.07)	5.94±0.16 (53.34±1.45)	2.44±0.25 (21.94±2.28)	7.50±0.31 (67.29±2.80)	0.56±0.10 (5.03±0.91)	30.56±0.30 (274.35±2.69)	49.61±1.29 (445.41±11.36)
			April	1.46±0.26 (12.26±2.16)	3.23±0.26 (27.09±2.20)	3.41±0.34 (28.60±2.85)	3.70±0.27 (30.96±2.28)	0.70±0.06 (5.86±0.47)	10.54±0.29 (88.24±2.41)	23.04±1.55 (193.01±10.23)
			July	1.73±0.18 (19.88±2.02)	2.65±0.25 (30.41±2.87)	4.09±0.14 (46.88±1.63)	3.40±0.32 (38.95±3.70)	0.56±0.16 (6.47±1.81)	5.11±0.20 (58.63±2.30)	17.54±0.33 (201.22±3.26)
10 (Sea water)	River mouth 1500 m south	41° 02′ 02″ N 13° 54′ 56″ E	November	1.29±0.10 (8.03±1.22)	1.69±0.11 (10.48±0.73)	4.13±0.19 (27.53±1.28)	2.41±0.19 (14.03±2.01)	1.01±0.10 (7.22±1.07)	25.85±0.20 (159.56±1.63)	36.38±0.28 (226.62±3.56)
			February	0.28±0.08 (3.54±0.92)	3.90±0.21 (51.49±2.41)	1.59±0.26 (18.49±2.96)	6.10±0.28 (79.24±2.65)	0.41±0.11 (5.21±1.32)	20.64±0.31 (247.52±2.94)	32.92±1.36 (405.49±11.32)
			April	1.23±0.21 (9.23±1.29)	1.97±0.12 (14.01±1.04)	2.97±0.19 (23.14±1.49)	2.86±0.10 (24.95±1.21)	0.46±0.09 (4.25±0.72)	7.93±0.24 (70.37±1.90)	17.42±0.35 (145.95±0.88)
			July	1.01±0.09 (7.54±0.54)	1.51±0.29 (10.79±2.20)	3.27±0.20 (25.52±1.54)	1.84±0.17 (12.39±1.21)	0.28±0.10 (2.29±0.70)	3.19±0.23 (31.11±1.76)	11.10±0.44 (89.64±2.55)

The samples were collected in triplicate

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average concentrations found in sediment samples were 3.33 ng g g^{-1} for HA and 3.26 ng g g^{-1} for ATR. Similarly, the mean concentrations observed for DPs in this study were comparable to those documented by Triassi et al. (DEA: 1.93 ng g^{-1}; DEHA: 1.75 ng g^{-1}; DIA: 0.81 ng g^{-1}; DIHA: 0.62 ng g^{-1})In this study the ratios of total amounts (sum of all concentrations obtained for single compound) found in WDP and SPM ([WDP]/[SPM]), as well as those of the total amounts determined in SPM and SED ([SPM]/[SED]) were estimated.

For both ratios the result was > 1, furthermore it was seen that the amounts of the compounds reduced from WDP to SED. In sediments, HA concentrations were higher than other metabolites, this can be justified by the chemical-physical characteristics of this DPs (low solubility and long half-life in soil). The findings indicated that chemical adsorption, which includes ion exchange and functional group complexation, is the primary factor influencing the adsorption of ATR by soil [57]. The H-bonding interactions between ATR and sediment are primarily responsible for the adsorption affinity of ATR to sediment [58].

Distribution mechanisms in the water system

The distribution mechanisms of ATR and its DPs from the Sele River was estimated by comparing the total concentration of samples collected at 10 sampling locations across four distinct seasons, both with and without rainfall. The seasonal variation patterns of these contaminants in WDP, SPM and SED were different (Fig. 3). Being the primary mode of transportation in the maritime environment, dissolved ATR is a priority concern, and the data obtained from monitoring conducted clearly showed an evident seasonal variations, when the value rises from summer months to rainy month and reaching the maximum values in February. It was evident that the greatest amounts were identified for WDP at the river mouth (96.56 ng L^{-1} in February) and gradually decreased from 58.4 ng L^{-1} at 500 m, to 50.7 ng L^{-1} at 1000 m and 46.2 ng L^{-1} at 1500 m south. All results are expressed as the average of the four seasons.

From the processing and evaluation of the data it is possible to deduce that the concentrations of ATR and DPs decrease considerably as one moves away from the mouth towards the sea, this could be explained by the dilution effect caused by sea water and other key factors such as temperature, dissolved oxygen and salinity (Table S3). The seasonal patterns that these environmental factors displayed help to explain the temporal changes in WDP, SPM and sediment. Temperature has an impact on ATR's environmental patterns, which include absorption, photodegradation, and biodegradation. The dissolved oxygen level is connected to the aerobic process

that forms DEA and DIA and eliminates side chains (ethyl and isopropyl groups). Salinity modified the pattern of fractionation among the WDP and the solid phase, which in turn changed the fluctuations in atrazine concentration. Overall, the results of this study showed that concentrations at various locations may be sensitive to the distances from the sample sites to the estuary, even though phase dispersion is one of the primary mechanisms of pesticide migration [59, 60].

Health risk assessment

The effects of ATR in human beings are not well known; nevertheless, as per findings by Swan et al. [61] and Swan [62], ATR and DPs were associated with a decline in semen quality and increased mortality among farmers exposed to them, in contrast to urban counterparts in the US. Moreover, elevated concentrations of ATR metabolites were detected in the urine of farmers engaged in the application of ATR in agricultural settings.

Hence, due to the hazardous properties associated with ATR, its usage has been prohibited in the European Union since 2003 [63]. Nonetheless, ATR and its DPs, including continue to be identified in aquatic environments.

According to Glinski et al. [64] and Velisek et al. [65], the DPs of ATR may exhibit greater toxicity compared to the parent compound and are frequently found in water bodies contaminated with pesticides. Consequently, the unregulated and illicit application of ATR poses a significant concern. Therefore, it is imperative to establish and enforce control measures to address this issue effectively.

Non-carcinogenic risk

Non-carcinogenic risk assessment involved calculating the Hazard Quotient (HQ), utilizing the mean values of ATR and DPs obtained to calculated the total Chronic Daily Intake [CDI ingestion + CDI dermal (Eq. 1 and 2)], in relation to the Reference Dose (RFD) [42]. ATR and its degradation products predominantly enter the human body through through contaminated water (WDP + SPM) and accidental ingestion.

The toxicity of ATR showed a direct correlation with its long-term daily use. This study examined the consumption rate through accidental ingestion and dermal contact with water and sediments, which may occur as a result of the potential uses of the river for both summertime recreational activities and agricultural purposes. Certainly, skin contact and inadvertent ingestion of surface water (from rivers and lakes) could potentially play a significant role in human exposure to these contaminants [66].

As indicated in the results presented in Table 4, the HQ levels were consistently below 1. This signifies that the concentrations of substances identified were below the

Table 3 Overview of the sampling area and mean concentrations (± standard deviations *n* = 3) of ATR and its metabolites in the April sediment sampling campaign of the Sele 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)	Sele River mouth	41° 01′ 19″ N 13° 55′ 26″ E	4.88±0.32	1.66±0.41	3.01±0.27	1.42±0.41	2.89±0.20	6.01±0.23	19.87±0.55
2 (seawater)	River mouth 500 m north	41° 01′ 05″ N 13° 55′ 38″ E	3.02±0.20	0.65±0.10	1.99±0.56	0.96±0.24	1.91±0.16	3.99±0.36	12.52±0.60
3 (seawater)	River mouth 1000 m north	41° 00′ 51″ N 13° 55′ 48″ E	1.99±0.18	0.32±0.10	1.25±0.22	0.70±0.17	0.99±0.12	2.26±0.25	7.51±0.22
4 (seawater)	River mouth 1500 m north	41° 00′ 33″ N 13° 55′ 49″ E	1.55±0.08	nd	1.07±0.04	0.15±0.01	0.69±0.15	1.26±0.09	4.72±0.10
5 (seawater)	River mouth 500 m west	41° 01′ 25″ N 13° 55′ 56″ E	4.01±0.23	0.70±0.35	2.00±0.12	1.36±0.24	2.48±0.23	4.01±0.28	14.56±0.77
6 (seawater)	River mouth 1000 m west	41° 01′ 00″ N 13° 54′ 52″ E	3.01±0.17	0.41±0.21	1.88±0.61	0.81±0.36	1.25±0.42	3.68±0.63	11.04±0.58
7 (seawater)	River mouth 1500 m west	41° 00′ 45″ N 13° 54′ 40″ E	2.88±0.31	0.36±0.07	1.33±0.21	0.21±0.05	2.23±0.29	2.87±0.69	9.88±1.01
8 (seawater)	River mouth 500 m south	41° 01′ 30″ N 13° 55′ 10″ E	3.87±0.26	1.10±0.15	2.25±0.11	1.32±0.51	2.85±0.39	4.52±1.12	15.91±1.35
9 (seawater)	River mouth 1000 m south	41° 01′ 47″ N 13° 55′ 05″ E	3.99±0.52	0.88±0.32	1.96±0.55	1.22±0.08	2.37±0.38	3.67±0.72	14.09±1.87
10 (seawater)	River mouth 1500 m south	41° 02′ 02″ N 13° 54′ 56″ E	3.72±0.71	0.66±0.21	1.89±0.39	0.77±0.43	1.48±0.35	3.56±0.59	12.08±0.69

The sediment samples were collected in triplicate

Nd not detected

limit associated with adverse impacts, suggesting a safe scenario.

Carcinogenic risk

Carcinogenic risks were evaluated for ATR and its DPs and it was calculated by multiplying total exposure (CDI) (µg/kg/day) and carcinogenic slope factor (SF) (kg*day/µg) [67].

In general, a risk value higher than 10^{-4} suggests unacceptable carcinogenic health risk, while a risk value of 10^{-6} could be reputed as the maximum acceptable level. So the risk value is between 10^{-6} and 10^{-4}, the health risk is reputed acceptable or tolerable [68] and that between 10^{-8} and 10^{-7} was reputed as negligible [69]. Accordingly, in this study we considered 10^{-6} as mean acceptable critical threshold for adults.

In this research, cancer risk for human in water (WDP + SPM) and sediment were reported in Table 4, data showed that there wasn't a cancer risk transfer the pollutants to the inhabitants by repeated consumption and skin contact in Sele River study area.

Environmental risk

To estimate the impact of the ATR and its DPs in the Sele River ecosystem, the HQ approach was used. The method was determined by comparing the maximum and mean measured concentrations of each contaminant with its corresponding lowest PNEC (extracted from the NORMAN ecotoxicology database) and to best reflect freshwater, marine water systems, native aquatic organisms from trophic levels of fish and aquatic invertebrates, were considered in this study.

The results obtained for the detected pollutants showed that none the compounds analyzed posed high environmental risk ($HQ_m > 10$) for the general-case scenario: ATR (HQ_m 0.003); HA (HQ_m 0.009); DEA (HQ_m 0.023) and DIA (HQ_m 0.044).

For the worst-case scenario, the HQ_{max}, using the maximum concentrations obtained, was calculated: ATR (HQ_{max} 0.0120); HA (HQ_{max} 0.060); DEA (HQ_{max} 0.240) and DIA (HQ_{max} 0.280). Again, none of the contaminants analyzed reported HQ_{max} values above 10, indicating that there is no possibility of high risk potential to be associated with chronic exposure to these pollutants in the Sele River. In addition the risk quotient of the ATR and DPs mixture (HQmix), estimated as the sum of the individual HQ_m values of each analytes, was 0.080, indicating a low environmental risk.

Based on the results obtained from this study it can be concluded that there is a low ecological risk in the Sele River estuary. In addition, metabolites DEA and DIA may be more hazardous than ATR [49], but the values
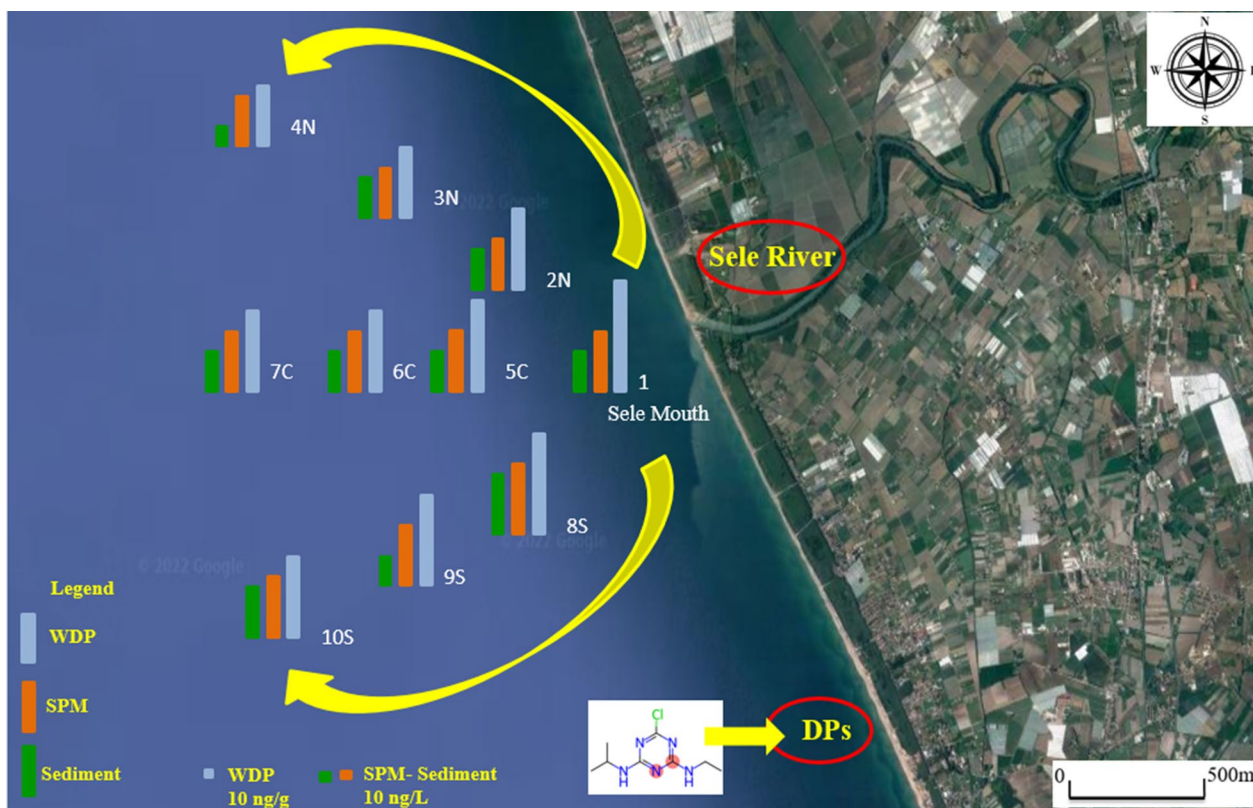
Fig. 3 Spatial distribution mechanism of ATR and DPs in the water system

Table 4 Non-carcinogenic risk and carcinogenic risk from ingestion and dermal routes

Compounds	Non-carcinogenic risk		Carcinogenic risk	
	Ingestion HQ	Dermal HQ	Ingestion ILCR	Dermal ILCR
WDP + SPM				
ATR	1.3×10^{-3}	8.7×10^{-8}	1.1×10^{-5}	7.0×10^{-10}
DIHA	9.9×10^{-4}	6.4×10^{-8}	7.9×10^{-6}	5.2×10^{-10}
DEHA	1.4×10^{-3}	9.6×10^{-8}	1.2×10^{-5}	7.7×10^{-10}
DIA	1.6×10^{-3}	1.0×10^{-7}	1.3×10^{-5}	8.6×10^{-10}
DEA	4.2×10^{-4}	2.7×10^{-8}	3.4×10^{-6}	2.2×10^{-10}
HA	7.5×10^{-3}	4.8×10^{-8}	6.1×10^{-5}	3.9×10^{-9}
Sediment				
ATR	9.4×10^{-2}	5.9×10^{-8}	7.4×10^{-6}	4.8×10^{-10}
DIHA	2.1×10^{-2}	1.3×10^{-8}	1.6×10^{-6}	1.1×10^{-10}
DEHA	5.3×10^{-2}	3.3×10^{-8}	4.1×10^{-6}	2.7×10^{-10}
DIA	2.5×10^{-2}	1.6×10^{-8}	2.0×10^{-6}	1.3×10^{-10}
DEA	5.4×10^{-2}	3.4×10^{-8}	4.3×10^{-6}	2.7×10^{-10}
HA	1.0×10^{-1}	6.4×10^{-8}	8.0×10^{-6}	5.2×10^{-10}

did not indicate worrying conditions for the species studied. Similarly, residues of ATR and HA did not present an unacceptable ecological risk.

However, many other factors need to be considered when assessing ecological risk, since aspects such as temperature, salinity, runoff, as well as temporal trends

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of exposure may influence the effects of pesticides and therefore, their risk to aquatic organisms.

Conclusions

The widespread use of pesticides has raised concerns worldwide due to their slow degradation and lasting presence, posing significant threats to environmental sustainability. This research provides valuable insights into ATR and its DPs pollution levels in the Sele River estuary. Water samples showed higher ATR levels compared to sediment samples, especially near the river mouth and exacerbated during winter due to increased rainfall. The study suggests contamination flowing southward into the Mediterranean Sea. Risk assessment in the Sele River area found that none of the samples exceeded contamination limits for ATR and its DPs, posing non-carcinogenic and carcinogenic risks, moreover the results obtained from the assessment of environmental risk demonstrated a low ecological risk in this area. This study is pioneering in assessing ATR levels in southern Italy's water and sediments despite its prohibition years ago. It highlights the ecological impact on the Mediterranean Sea, providing crucial data for water contaminant legislation and standards.

Abbreviations

ATR	Atrazine
DPs	Degradation products
WDP	Water dissolved phase
SPM	Suspended particulate matter
DEA	Desethylatrazine
DIA	Desisopropylatrazine
HA	Hydroxyatrazine
DEHA	Desethylhydroxyatrazine
DIHA	Desisopropylhydroxyatrazine
SED	Sediment
CDI	Chronic daily intake
HQ	Hazard quotient
ILCR	Incremental Lifetime Cancer Risk

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s12302-024-00941-6.

> Supplementary Material 1.

Declarations

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