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A quality index-based methodological perspective to assess surface water geochemical evolution under global change and increasing anthropogenic pressures

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ABSTRACT

Effective and sustainable water management is a major challenge under global change and increasing human pressures. Developing reliable and user-friendly tools is essential to evaluate water quality over time and space and to support decision-making. This study presents the application of the recently developed Chemical Water Quality Index (CWQI), a methodological framework designed to provide a simple, flexible, and widely applicable approach for quantifying water quality. The main objectives were to: (i) track the evolution of water chemistry along the river course, (ii) assess the contribution of different solutes to overall quality, (iii) detect contamination hotspots, and (iv) explore long-term trends in relation to environmental policies. The approach was tested on the Arno River Basin (Tuscany, Italy), one of the largest and most impacted catchments in central Italy, using published geochemical data from four periods (1988–1989, 1996–1997, 2002–2003 and 2017). Results indicate good to fair quality in upstream reaches, with clear deterioration downstream of Florence, primarily linked to chloride, sodium, and sulphate inputs from urban, industrial, and agricultural activities. Despite increasing anthropogenic pressures, water chemistry remained relatively stable over three decades, suggesting that regulatory measures helped to prevent further degradation. Beyond this case study, the CWQI represents an operational tool that can be readily applied in different contexts. Future developments should be aimed at overcoming some limitations and including integration with biological indicators and the use of longer, high-resolution datasets to capture seasonal variability, separate natural from anthropogenic drivers, and provide stronger support for sustainable river management.

1. Introduction

It is well acknowledged in the scientific world that climate change represents a major environmental and social challenge that humanity must face in the upcoming decades. The effects of global change, e.g., rising temperature and intensification of extreme events such as droughts and floods, are severely endangering natural environments. Riverine systems are highly sensitive to environmental changes and external forcing (e.g., Whitehead et al., 2009; D'Oria et al., 2019; Salerno et al., 2018; Borretti and Rosa, 2019; Burri et al., 2019; Barbieri et al., 2023; FAO, 2023; WHO, 2024; Taucare et al., 2024). Surface waters reflect the integrated outcome of multiple processes, including water–rock interaction, soil run-off, precipitation inputs, biological activity, and biogeochemical cycling, upon which anthropogenic human pressures are superimposed. Such pressures, including agriculture, industrial activities, and urbanization, contribute to discharge organic, inorganic, and/or biological pollutants, often making the water unfit for drinking and exposing populations to severe health risks (Barikdere et al., 2010; Deblonde et al., 2011; Schullehner et al., 2018; Gupta et al., 2021; Morin-Crini et al., 2022). Therefore, climate change and increasing anthropogenic impacts are strongly jeopardizing the water resource at global and local scales, in terms of both quantity and quality

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(Burri et al., 2019; Gupta et al., 2021; Sarker et al., 2021; FAO, 2023; Taucare et al., 2024; Taussi et al., 2024). Consequently, the sustainable and effective management of water resources represents a pressing issue that requires immediate and effective action worldwide.

In water and environmental sciences, water quality indexes (WQIs) are commonly used as tools to evaluate the overall quality of the water resources taking into account different parameters (e.g., chemical, biological) and using various mathematical and computational approaches (e.g., Horton, 1965; Brown et al., 1970, 1973; Prati et al., 1971; Dinus, 1987; Saffran et al., 2001; Vasanthavigar et al., 2010; Kachroud et al., 2019; Uddin et al., 2021; Centeno et al., 2023; Chemeri et al., 2023). In this paper, we introduce a simple and efficient methodological approach to evaluate and quantify the environmental impact of different compounds in surface waters based on the application of the *Chemical Water Quality Index* (CWQI) (Chemeri et al., 2023). Hence, this approach aims at assessing the water chemistry as a function of its quality evolution along a river course, and evaluating the contribution of different solutes in affecting (and compromising) the chemical quality of surface waters. Besides, it can help in identifying contaminated areas, evidenced by major CWQI increases, or highlighting those subjected to a possible chemical risk, and unravelling how water quality has been changing over the years in response to environmental changes, urban expansion, and legislative or mitigation measures, such as the Water Framework Directive (WFD). To illustrate the practical application of this methodology, case studies in well-documented river basins are essential, as they allow global challenges to be examined at a local scale. The Arno River Basin (ARB, Tuscany, Italy), the second largest river basin in central Italy, represents an ideal case study due to: (i) its long-term (non-continuous) monitoring datasets spanning nearly 30 years and (ii) the significant human influence (i.e., agriculture, nursery, industrial activities) along its catchment as it flows across many large cities, e.g., Florence, Pisa and Arezzo (e.g., Bencini and Malesani, 1993; Cortecci et al., 2002, 2009; Nisi et al., 2005, 2008a; Chemeri et al., 2026). By applying the proposed approach in the ARB, we can capture how environmental pressures and human activities can influence a river system and evaluate the effectiveness of integrated water quality assessment approaches.

The study focused on previously published literature data by selecting the same sampling sites (11 in the main catchment and 8 river tributaries) that were analysed in four different time frames (1988–1989, 1996–1997, 2002–2003, and 2017). The computed CWQI values included pH, electrical conductivity, hardness, sodium, chloride, sulphate, potassium and nitrate across both spatial and temporal dimensions. Moreover, the spatial analysis specifically relied on the dataset of Nisi et al. (2008b), which provided excellent spatial coverage with 220 sites across the entire basin, including smaller tributaries, ensuring a robust assessment of spatial changes. The ultimate objective of this study is to present an operationally efficient and methodologically robust approach for processing and interpreting geochemical data, offering a practical and accessible tool for agencies and professionals engaged in environmental management and monitoring.

2. Methodology

2.1. Water quality indexing and CWQI strengths

Water quality indexing is a common practice when dealing with water management. Water quality indexes (WQIs) allow the aggregation of multiple parameters (e.g., major components, trace elements, biological data) into a single value that summarizes the qualitative status of the water resource (Kachroud et al., 2019; Uddin et al., 2021). However, most indexes show several flaws and inconsistencies that are limiting their applicability and may lead to errors in the final assessment of water quality (Kachroud et al., 2019). The main problematics are related to: (i) a complex mathematical computation; (ii) the selection of the variables and the lack of inclusivity, since most of the indexes are based on a fixed number of parameters and prevent the inclusion of additional ones (e.g., Horton Index, NSF-WQI) which is extremely important considering the potential impact of emerging chemical pollutants (e.g., pesticides, pharmaceuticals) (Uddin et al., 2021; Chemeri et al., 2023); (iii) the weightage method, since an incorrect weight assignment can affect the entire calculation, generating an eclipsing problem and producing unreliable results (Ott, 1978; Uddin et al., 2021 and therein references); and (iv) site-specificity and water body dependence, since some indexes can be only applied in a given study area and/or to a specific water body (e.g., to surface waters and not to groundwater) (Kachroud et al., 2019; Uddin et al., 2021; Centeno et al., 2023; Chemeri et al., 2023). *The Chemical Water Quality Index* (CWQI) was developed to overcome these criticalities and provide a simple and effective computation methodology. Indeed, the CWQI is characterized by a simple mathematical computation easily manageable on Excel (see Section 2.2 for the detailed description) and introduces a weightage method that strongly reduces the eclipsing problem. For further details, we refer to Chemeri et al. (2023). Additionally, the CWQI is an "*open*" index that allows the inclusion of any parameter (e.g., chemical, physical and biological) at users' discretion and/or based on data availability. Finally, its accuracy and reliability were calibrated and tested on a wide number of waters, coming from different hydrogeological and geodynamic settings, during its development (>1800 computations), also confronting the CWQI outcomes with those produced with different indexes, and corroborated by recently published studies related to both ground- and surface waters (e.g., Taussi et al., 2024; Chemeri et al., 2026). In fact, the CWQI outcomes showed a strong correlation with the number of variables exceeding the quality target ($r = 0.94$) (Chemeri et al., 2023), thus supporting the reliability and robustness of the results obtained. Furthermore, the testing phase also allowed to overcome the site-specificity and water body dependence, making the CWQI an effective operational tool applicable to any kind of water in every possible environment.

2.2. Overview on the CWQI computation

Here, we present an overview on the main steps to calculate the CWQI values. For a detailed description on the CWQI development and computation process, we refer to Chemeri et al. (2023).

After the selection of the variables, the first step of the CWQI calculation consists in a *transformation* phase, where a score (s), from ~1 to 10, is assigned to each variable based on the measured value/concentration and quality targets, following Eqs. (1) and (2).

$$s = \frac{10}{1 + 6.714e^{2.234(0.148 - a)}}; \quad a = \frac{\textit{measured value}}{\textit{reference value}} \quad (R^2 = 0.94) \tag{1}$$

$$s_{pH} = \frac{10}{1 + 1.953e^{6.381(0.985 - b)}}; \quad b = |7.5 - pH_{measured}| \quad (R^2 = 0.93) \tag{2}$$

Reference values are represented, in our case, by the European quality standards for drinking waters (Directive 2020/2184/EC, 2020).

In detail, the score equals 5 when the measured value equals the reference one (i.e., $a = 1$ in Eq. (1)) or in the case of Eq. (2), when b equals 1, indicating that the measured value coincides with the minimum or maximum value of the acceptable range. Hence, the higher the score, the higher the impact of the selected variable in compromising the overall quality (Chemeri et al., 2023). The transformation (or *parametrization*) phase gives to the method two strong advantages: (a) it brings all the variables to a common scale, represented in this case by the score (s), hence allowing to compare different parameters that may be reported in different units of measurement (e.g., pH, EC, dissolved solids) or that may be covering different ranges (e.g., major components in mg/L and trace elements mostly expressed in μg/L), and additionally, (b) it permits to the score to provide information regarding the content (or value) of the variable relative to a target value and also gives a prompt insight on the influence that a parameter may have on water quality.

Table 1
The CWQI classification and the possible water use are presented (Chemeri et al., 2023).

CWQI value	Ranking class	Possible use
≤2.00	good	*water may be considered for drinking purposes, upon microbiological analyses*
2.01–4.00	fair	*water may be considered for irrigation or industrial usage, water may be evaluated for drinking purposes, upon microbiological analyses and treatment is necessary (e.g., dilution, purification)*
4.01–6.00	poor	*water not suitable for drinking purposes, other uses may be evaluated depending on elements concentrations*
6.01–8.00	very poor	*water quality is extremely damaged, the use is not recommended.*
8.01–10	extremely poor	*water quality is irreversibly damaged, the use is not recommended.*

The following step is the *weightage*, where a weight (w) is assigned to each parameter, directly proportional to the score (s) obtained in the previous step, according to Eq. (3).

$$w_x = \frac{s_x}{\sum_{i=1}^{n} s_i} \tag{3}$$

Moreover, the overall contribution of each single parameter (x) to the water quality may be reported as *influence (or impact) factor* (IF_x), which is given by the value of the weight (or by the sum of the weights if a group of components is considered) recalculated to one-hundred (%) according to Eq. (4), as reported in Chemeri et al. (2026).

$$IF_x = 100^* w_x = 100^* \frac{s_x}{\sum_{i=1}^{n} s_i} \tag{4}$$

Eventually, the index is computed by aggregating together scores and weights to come out with a single number that summarizes the overall water quality status, following Eq. (5).

$$CWQI = \prod_{i=1}^{n} s_i^{W_i} \tag{5}$$

The CWQI ranges between ~1 (very good chemical quality) and 10 (extremely poor chemical quality); specifically, five quality ranking classes were identified: *good* (<2), *fair* (2.01–4), *poor* (4.01–6), *very poor* (6.01–8) and *extremely poor* (8.01–10) (Table 1) (Chemeri et al., 2023). The numerical categorization allows a quick and reliable assessment of water quality that may favour water management practices (Chemeri et al., 2023, 2026; Taussi et al., 2024).

2.3. Proposed approach and management of the dataset

The methodological framework applied in this study relies on the Chemical Water Quality Index (CWQI) to investigate spatial, temporal, and combined spatial–temporal trends of surface water quality. CWQI values, together with single-variable scores (s_x) and influence factors (IF_x), were used to identify chemically compromised stretches, highlight potential sources of contamination, and evaluate changes over time in relation to environmental policies and land-use transformations. As previously mentioned, the approach was tested in ARB, which was selected for the availability of (four) extensive geochemical datasets spanning nearly 30 years (1988–2017) and covering both the main course and tributaries (Table 2) and also due to the fact the ARB surface waters flow within areas characterized by a relatively strong anthropogenic pressure which is influencing water geochemistry (Nisi et al., 2008a, 2008b). Nineteen sites were considered in total (11 along the Arno River and 8 related to in major tributaries) (Table 2b, Fig. 1), with sampling campaigns carried out in different seasons to capture potential

Table 2
(a) List of the previously published studies focusing on the Arno River Basin (ARB), time frame and number of sampling surveys were also reported; (b) list of the selected sampling sites: ID, full name (and *river*), distance from the source (in km) and number of total analysis available are reported.

(a)

reference	**temporal frame**	**referred in this study as**	**number of sampling surveys**
Bencini and Malesani (1993)	1988–1989	T_1	3
Cortecci et al. (2002)	1996–1997	T_2	up to 4
Nisi et al. (2005, 2008a,b)	2002–2003	T_3	up to 6
Chemeri et al. (2026)	2017	T_4	1

(b)

sample ID	**full name (*river*)**	**distance from the source (km)**	**N (*total analysis*)**
AR-1	Stia/La Casina (*Arno*)	12.5	14
AR-2	Rassina (*Arno*)	35.0	12
AR-3	Ponte Buriano (*Arno*)	60.5	12
AR-4	Laterina (*Arno*)	69.5	12
AR-5	San Giovanni Vld. (*Arno*)	88.0	12
AR-6	Rignano sull'Arno (*Arno*)	109.5	9
AR-7	Rosano (*Arno*)	118.0	14
AR-8	Empoli (*Arno*)	168.5	12
AR-9	Castelfranco (*Arno*)	188.0	11
AR-10	Ponte Navetta/Pontedera (*Arno*)	200.0	9
AR-11	Pisa (*Arno*)	232.0	11
T-Ch	Ponte ai Chiani (*Chiana*)	64.0	6
T-Si	Pontassieve (*Sieve*)	117.0	12
T-Om	Comeana/Carmigano (*Ombrone*)	151.0	13
T-Pe	Montelupo (*Pesa*)	161.0	11
T-El	Ponte a Elsa (*Elsa*)	176.0	13
T-Eg	Ponte a Egola (*Egola*)	182.0	12
T-Us	Montecalvoli (*Usciana*)	192.0	13
T-Er	Pontedera (*Era*)	202.0	13

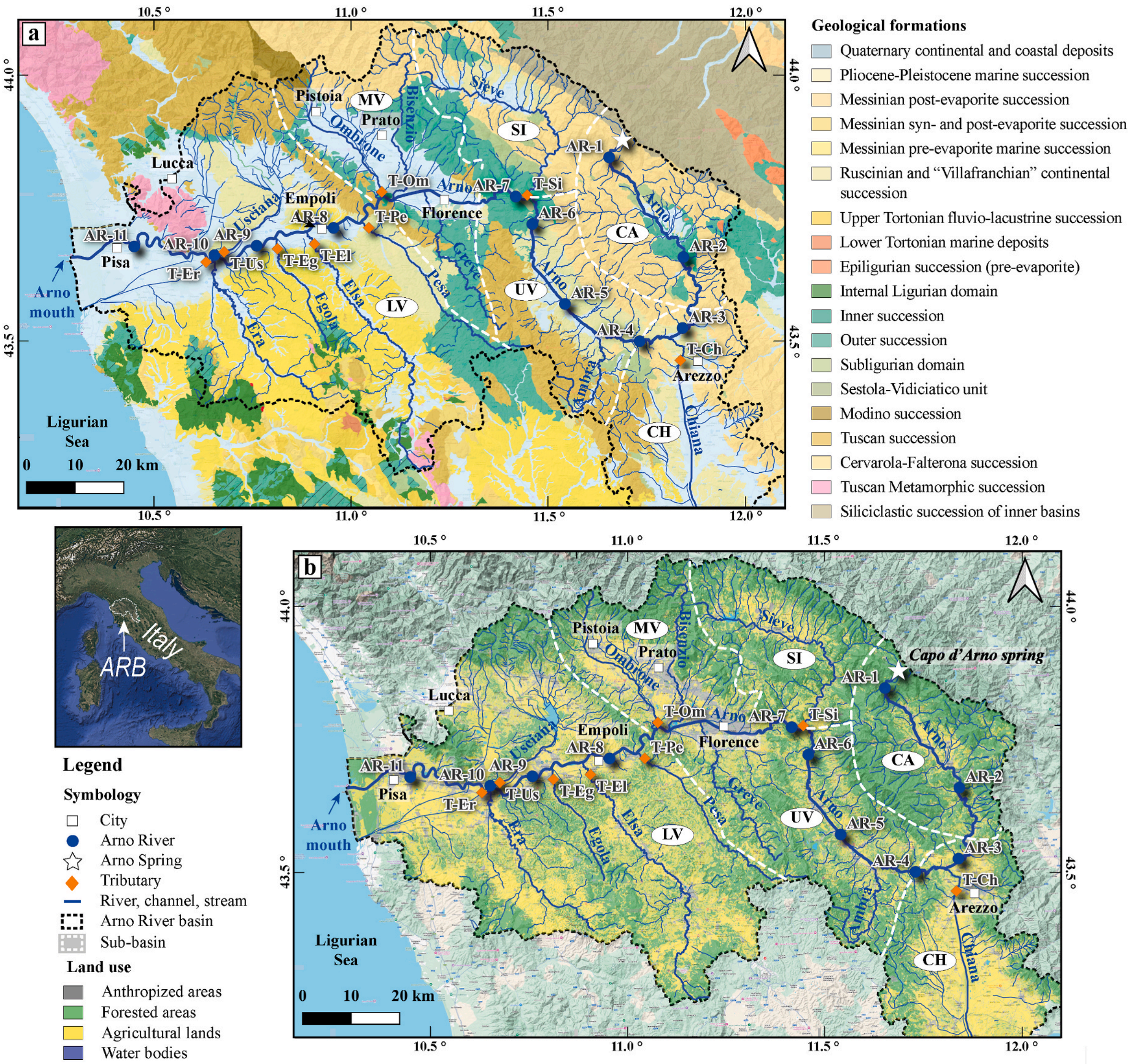

Fig. 1. (a) Geological (after Conti et al., 2020) and (b) land use (after Regione Toscana, 2019) maps of the Arno River Basin (ARB) The location of the sampling sites described in Table 2 is also reported. The Arno River catchment is divided into six sub-basins, as follows: Casentino (CA), Chiana (CH), Sieve (SI), Upper Valdarno (UV), Middle Valdarno (MV) and Lower Valdarno (UV). The location of the Arno Spring (Capo d'Arno) and the main cities are also reported on the map.

seasonal variability (the full datasets are reported in Supplementary Material 1). In detail: (i) for the 1988–1989 dataset (referred in this study as T_1) the sampling surveys were performed in September 1988, February 1989 and April 1989 (Bencini and Malesani, 1993), (ii) for the 1996–1997 (referred as T_2), samples were collected on a quarterly basis from November 1996 to October 1997 (Cortecci et al., 2002), (iii) data from Nisi et al. (2005, 2008a,b) (T_3 in this study) span from May 2002 to October 2003 and analysis were performed quarterly or every four months (see Supplementary Material 1), and (iv) for the most recent dataset (T_4), the sampling was conducted in September 2017 (Chemeri et al., 2026). Further details on the sampling periods (dd/mm/yyyy) and on rainfalls for the previous 30 days (before sample collection) are reported in the Supplementary Material 2. Additional details on the main features of the ARB are reported in the following subparagraph.

For each site, the CWQI values were calculated including pH, electrical conductivity, hardness (as a function of Ca and Mg), chloride, fluoride, sulphate, nitrate, sodium, and potassium, using the EU standards for drinking water (Directive 2020/2184/EC, 2020) as reference. It is worth mentioning that the European Directive does not regulate the content of K in drinking waters. However, the World Health Organization (WHO, 2009) highlighted that excessive potassium intake can represent a health concern, particularly for individuals with impaired renal function, and suggested an upper acceptable limit of 80 mg/L in drinking water. Since values approaching the WHO limit were found in the ARB, K was included in the computation. In addition to its relevance for human health, elevated K concentrations may also act as indicators of anthropogenic influence, as they are often linked to the application of potassium-based fertilizers and other agricultural inputs (e.g., Melo et al., 2012). Thus, the inclusion of potassium in the index is justified both from a public health perspective and as a potential tracer of human impact on surface water quality. It should be noted that NO_3 contents were not available for the earliest dataset (T_1: 1988–1989) and could not be included in the computation. This absence represents a limitation and may slightly bias the comparison with subsequent periods. However, previous studies (Chemeri et al., 2026) have shown that nitrate exerts a relatively low and limited influence on water quality in the ARB (IF_{NO3} $\approx$ 6 %) when compared to other parameters. Therefore, while caution is needed when comparing T_1 with later periods, the absence of nitrate does not substantially affect the overall CWQI trends calculated for T_2 (1996–1997). T_3 (2002–2003) and T_4 (2017). In detail, three types of analysis were performed:

- *spatial trends*, based on the spring 2002 survey of Nisi et al. (2008b), which included 220 sites providing a wide spatial coverage; additional parameters were also considered in the computation (B, NO_2, NH_4);
- *temporal trends*, focusing on the Sieve (T-Si), Ombrone (T-Om), and Usciana (T-Us) tributaries, since the latter two showed a variable behaviour in previous studies and strong influence from anthropogenic activities while T-Si was considered a reference "*end-member*", being mainly influenced by geogenic/natural processes and less affected by human pressures. In this computation, for T-Us and T-Om 13 complete analysis were available (2 for T_1, 4 for T_2, 6 for T_3 and 1 for T_4) while 12 sampling surveys were performed for T-Si (2 for T_1, 4 for T_2, 5 for T_3 and 1 for T_4) (Table 2). Full details and results are reported in the Supplementary Material 1.
- *spatial–temporal trends*, along the Arno main course (AR-1 to AR-11), using mean CWQI values across the four time frames (T_1–T_4). The number of total observations available for each sampling site ranged from 9 (AR-6) up to 14 (AR-7) (Table 1; Supplementary Material 1).

2.3.1. Geological, hydrological and anthropogenic features of the Arno River Basin

The ARB is predominantly distributed within the region of Tuscany (98.4 %) and marginally in that of Umbria (1.6 %). It encompasses a total area of 8228 km^2 and has a mean elevation of approximately 353 m a.s.l. The Arno River originates from the *Capo d'Arno spring* on the southern slopes of Mt. Falterona (Northern Apennines) at an altitude of 1385 m (Fig. 1). From its source, the Arno flows for 242 km, traversing notable urban centres including the UNESCO World Heritage city of Florence, before ultimately discharging into the Ligurian Sea, about 10 km west of Pisa (Fig. 1). The geological framework of the ARB is predominantly characterized by sedimentary formations of Mesozoic and Tertiary age, which have undergone folding and faulting due to the orogenic processes associated with the development of the Apennine Chain (Fig. 2) (e.g., Abbate et al., 1992; Cortecci et al., 2002; Nisi et al., 2008a and references therein). During the Pleistocene, the area experienced an extensional tectonic phase that led to the formation of a NW–SE-oriented horst and graben system. The structural configuration influenced the current drainage pattern of the Arno River and delineated six principal sub-basins: Casentino (CA), Chiana Valley (CH), Sieve (SI), Upper Valdarno (UV), Middle Valdarno (MV), and Lower Valdarno (LV) (Fig. 1) (Baldacci et al., 1967; Carmignani and Kligfield, 1990).

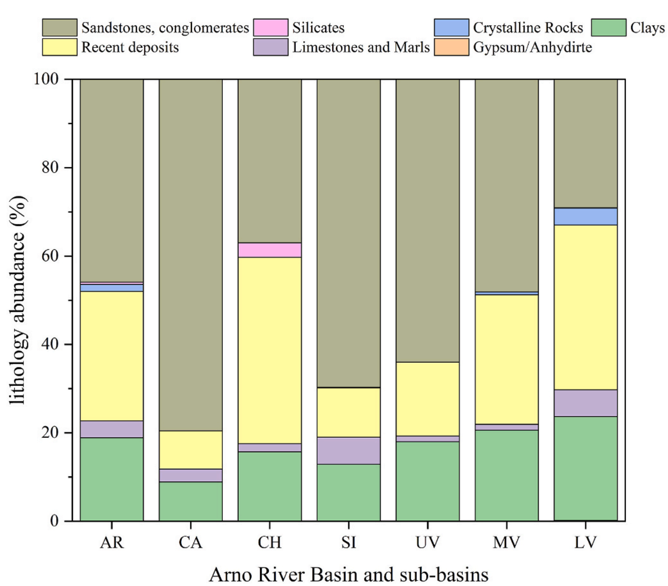

Fig. 2. Bar graph of the simplified geology for the main basin (AR) and six sub-basins (CA, Casentino; CH, Chiana; SI, Sieve; UV, Upper Valdarno; MV, Middle Valdarno; LV, Lower Valdarno). The abundance of each lithology is given in %. Values are reported in the Supplementary Material 3. Data from Regione Toscana (2019).

In the upper sector of the Arno River Basin, the lithology is mainly dominated by siliciclastic turbiditic formations (Fig. 2), i.e., the Cervarola-Falterona and Macigno formations, which are prevalent near the river's source area. The Chiana Valley, by contrast, is mainly composed by Pliocene continental and lacustrine marl deposits. Similarly, the upstream portion of the Sieve sub-basin is largely characterized by sandstone units. However, several springs that feed the Sieve River are sourced from calcareous lithologies associated with the Ligurian Flysch complex (Fig. 2) (Cortecci et al., 2002; Nisi et al., 2008a). Downstream of Florence, the Bisenzio, Ombrone, and Usciana rivers, which are right-bank tributaries of the Arno, flow through the Macigno Formation. In contrast, the left-bank tributaries, including the Greve, Pesa, Elsa, Egola, and Era rivers, primarily drain Pliocene to Quaternary marine and lacustrine clayish and sandy deposits (Fig. 2) (Cortecci et al., 2002 and references therein). In the upper reaches of the Elsa and Era basins, Triassic and Messinian evaporites outcrop. In the final section of its course, the Arno River crosses the coastal plain near Pisa, which is predominantly consisting of recent alluvial deposits (Fig. 2) (Cortecci et al., 2002, 2009; Nisi et al., 2008a). Noteworthy is the fact that both the Ambra and Elsa rivers are influenced by the discharge of thermo-mineral springs, with temperatures up to 45 °C, along their courses (Nisi et al., 2008a, 2008b).

The ARB exhibits a rainfall regime with a peak in autumn, specifically in October and November (ca.140 mm). Precipitation gradually decreases from January onward, reaching its lowest values in the summer months (July and August, <40 mm). The complex orography of the region determines a significant spatial variability in the precipitation patterns in the different sub-basins (Giani and Panichi, 2003 and reference therein). The hydrometric regime of the river shows notable fluctuation, with discharge peaking in December at ~60 m^3/s and reaching its lowest levels in August and September (ca. 10 m^3/s). The Arno River is characterized by a predominantly torrential nature before Arezzo, primarily due to the low catchment storage capacity, which is attributed to the predominance of impermeable soils, particularly in the Casentino and Sieve sub-basins (Fig. 1), which are major contributors to the river flow (Giani and Panichi, 2003).

The Arno River flows through urban, industrial and agricultural areas (Fig. 1), which exert a significant anthropogenic pressure on the river (Table 3), as documented by Bencini and Malesani (1993), Cortecci et al. (2002, 2009), Nisi et al. (2005, 2008a) and Chemeri et al., 2026. To date, it includes: (a) substantial impacts from agricultural and zootechnical activities, particularly in correspondence of the confluence with the Chiana tributary, where untreated wastewaters enter the river; (b) discharge of treated and/or partially-treated domestic sewage from Florence; (c) release of industrial wastewaters, mostly from textile production and nursery activities in the Prato and Pistoia areas, throughout the Bisenzio and Ombrone tributaries; (d) discharges from tanneries and paper mills upstream of Pisa, where partially treated effluents are discharged by the Usciana channel and smaller tributaries (Tognotti et al., 1998; Maccelli, 2025). A further quality-endangering factor, not ascribable to human activity, is represented by the intrusion of seawater in the river final stretch, with the saline wedge sometimes extending up to 27 km inland due to west winds (Bencini and Malesani, 1993; Cortecci et al., 2002; Nisi et al., 2005, 2008a; Chemeri et al., 2026).

It is noteworthy to point out that over the last decades (including the time of our study) (Table 3), the longstanding anthropogenic impacts on the Arno Basin has undergone significant demographic, urban, and industrial transformations (Nisi et al., 2008a, 2008b; Alberti and Paloscia, 2018). The population density in the basin has increased, particularly in the metropolitan area of Florence, leading to higher urbanization rates and further development of industrial zones. These demographic shifts have been paralleled by a rise in land consumption, with agricultural

Table 3
Temporal evolution of land use in the Arno River Basin (ARB) and the Sieve (Si), Ombrone (Om) and Usciana (Us) sub-basins from 1990 to 2018 (Regione Toscana, 2019). The simplified land use is reported in % as anthropized areas (AA, including cities, industrial areas, roadways, railways, airports and construction sites), agricultural land (AL), forested land (WL) and water bodies and wetlands (WW). The relative percentage change (±) between 1990 and 2018 is also reported.

ARB	AA	AL	WL	WW	Si	AA	AL	WL	WW
1990	5.1	52.9	41.3	0.6	1990	2.0	32.9	65.0	0.1
2000	5.7	52.3	41.4	0.7	2000	2.3	32.0	65.2	0.5
2006	6.2	51.9	41.3	0.6	2006	2.7	31.8	65.0	0.5
2012	6.9	51.9	40.5	0.8	2012	2.9	32.2	64.4	0.5
2018	6.9	51.9	40.5	0.7	2018	2.8	32.2	64.4	0.5
+/−	**+34.0**	**−2.0**	**−1.9**	**+19.9**	+/−	**+39.8**	**−1.9**	**−0.9**	**+597.8**
Om	AA	AL	WL	WW	**Us**	AA	AL	WL	WW
1990	12.7	50.5	36.6	0.2	1990	7.9	53.7	35.8	2.6
2000	14.3	48.9	36.6	0.3	2000	8.6	53.0	35.8	2.6
2006	15.1	48.0	36.6	0.3	2006	9.7	51.9	35.8	2.5
2012	17.0	47.7	34.6	0.7	2012	10.7	53.6	33.2	2.6
2018	17.0	47.7	34.1	1.2	2018	10.7	53.6	33.2	2.6
+/−	**+33.7**	**−5.6**	**−6.9**	**+508.6**	+/−	**+35.9**	**−0.3**	**−7.4**	**−0.6**

and forested areas being increasingly converted to urbanized zones (Table 3), infrastructure, and industrial complexes (Alberti and Paloscia, 2018 and therein references). In fact, between 1990 and 2018, those areas dedicated to human-related activities (such as urban conglomerates and industrial zones) have been recording a relative increase of 34 % and leading to a 2 % decrease in the extent of both agricultural and forested areas, respectively (Table 3). The expansion of residential areas and the establishment of new commercial and industrial districts have contributed to intensifying and increasing pressures on water resources, with growing demands for water treatment and waste management systems. The population within the Arno River Basin is ~2.5 million, but the level of anthropogenic pressure is equivalent to that of 8.5 million people (Nisi et al., 2008b). Furthermore, changes in land use have affected local hydrology, with increased impervious urbanized areas, reducing the natural water retention capacity of the landscape and contributing to higher flood risks (Morelli et al., 2012; Lu et al., 2015). This ongoing urban and industrial development has compounded challenges of managing the river water quality and ecological health, necessitating ongoing attention to both the prevention of pollution and the enhancement of urban water management systems (Nisi et al., 2008a, 2008b; Morelli et al., 2012).

3. Results and discussion

3.1. Spatial trends and contaminated areas

The computation of the spatial trends was performed on the dataset presented by Nisi et al. (2008b), which is referred to a large-scale

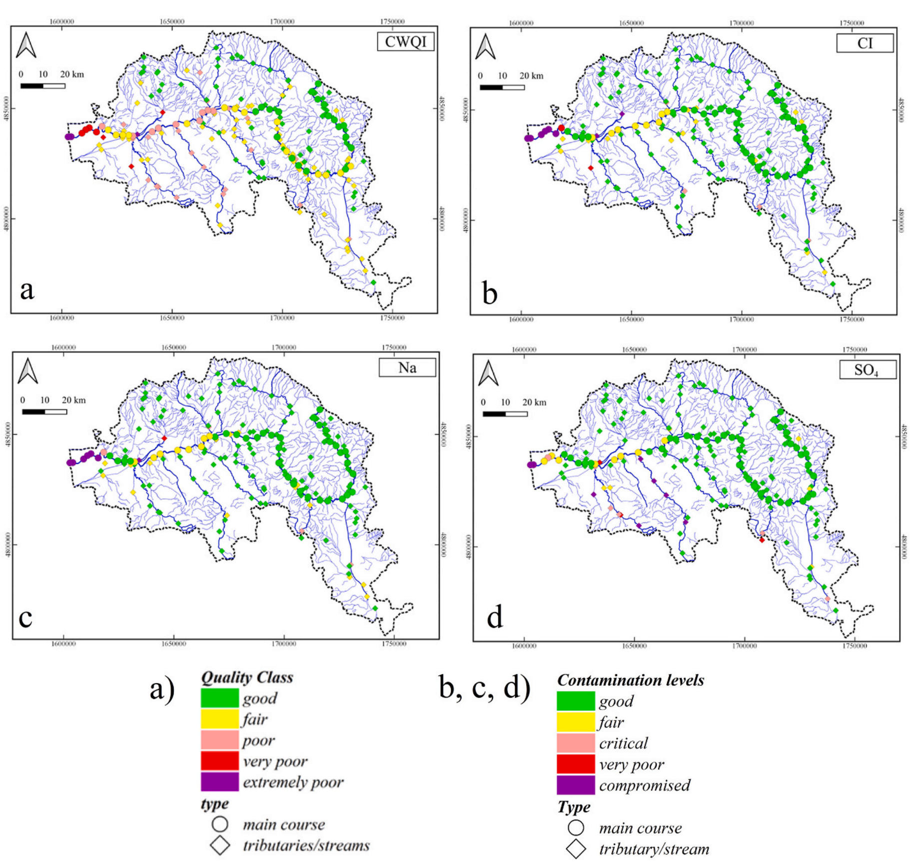

Fig. 3. Quality spatial trends in the Arno River Basin for (a) CWQI, (b) chloride (Cl), (c) sodium (Na) and (d) sulphate (SO_4). Quality classes for the CWQI and contamination levels for Cl, Na and SO_4 according to the ranking proposed in Chemeri et al. (2023) are reported in the legend.

sampling campaign covering the entire ARB, including the main catchment, major and minor tributaries, carried out during spring 2002. The study involved a total of 220 sampling points. The CWQI was calculated including eleven parameters, namely, pH, EC, Cl, SO_4, Na, hardness, F, B, NH_4, NO_3 and NO_2. The full dataset and the results obtained are reported in the Supplementary Material 4. For further details the reader can refer to Nisi et al. (2008b).

The CWQIs are plotted on the ARB map in Fig. 3a. The results show that the ARB running waters are characterized by a good-to-fair quality in the first part of its course, specifically upstream of the city of Florence, for ~130 km. A decrease in the water quality is evident downstream. The ARB waters flowing towards the Middle and Lower Valdarno are in most cases showing poor quality (CWQI >4) (Fig. 3a). The worsening in quality reflects the crossing of areas characterized by intense anthropogenic activity (e.g., the Firenze-Prato-Pistoia plain and the Lower Valdarno tanning districts; Fig. 1) as well as the input of tributaries, which are also highly subjected to pollution related to human practices. However, it must be noted that the quality deterioration detected in the Elsa River, being characterized by a Ca(Mg)-SO_4(HCO_3) composition, is related to the discharge of thermo-mineral springs originated from the interaction with the Burano Fm, hence it has to be considered as a case of geogenic contamination. In the terminal part, the CWQI values rise above 6, indicating a very or extremely poor quality (Fig. 3a). The CWQI increments detected at the mouth of the Arno River are due to seawater intrusion, as widely documented by Bencini and Malesani (1993), Cortecci et al. (2002) and Nisi et al. (2008a,b). Hence, as the Arno River flows through the Middle and Lower Valdarno, a clear deterioration in water quality is observed. This decline coincides with a marked increase in urban land use—over 13 % and 11 %, respectively—compared to the less urbanized Upper Valdarno. The correlation suggests that the intensifying anthropogenic pressure, including urban runoff, wastewater discharges, and habitat alteration, plays a key role in degrading water quality. The CWQI data highlight how urban expansion directly influences the river's chemical health.

As expected, along their courses, the tributaries show similar trends to those observed for the main catchment with their quality decreasing as approaching the confluences (Fig. 3a). Hence, the application of the spatial trends provides useful insights into both the water geochemical evolution along the main courses and the identification of the most contaminated stretches, represented, for the Arno River, by the Middle and Lower Valdarno (Fig. 2a). Referring to the tributaries, the high-(chemical)-risk areas are represented by the confluence of the Arno River with the Elsa, Era, Ombrone and Usciana rivers (Fig. 1), since they carry in the main catchment chemically- and qualitatively-compromised waters, due to high contents in Cl, Na and SO_4 (as reported in the Supplementary Material 1). Since the CWQI provides the overall quality, to identify the impact of a single species (or compound), the same approach can be performed considering the trends of their scores (Fig. 3b, c, d), calculated according to Eqs. (1) and (2). The impact of Cl on water quality (Fig. 3b) is generally low along the first section of the Arno River, i.e., upstream of Florence, with a slight quality decrease in the Middle Valdarno and a strong increase in its score, towards very and extremely poor ratings, approaching the river mouth, as the saline wedge enters the main course particularly when SW winds are blowing (e.g., Bencini and Malesani, 1993). Critical contents ($4 < s_{(Cl)} < 6$) in chloride can also be found in the upper reaches of the Ambra and Elsa tributaries due to the influence of thermo-mineral springs, with a consequent lowering of the $s_{(Cl)}$ downstream towards optimal conditions ($s_{(Cl)} < 2$) following dilution processes (Nisi et al., 2008a, 2008b), and in the final course of the Ombrone river, right before its confluence in the Arno River (Fig. 3b). Chemically compromised conditions for chloride contents are also found in the final part of the Usciana channel ($s_{(Cl)} > 8$).

A similar behaviour is detected for Na with its higher scores

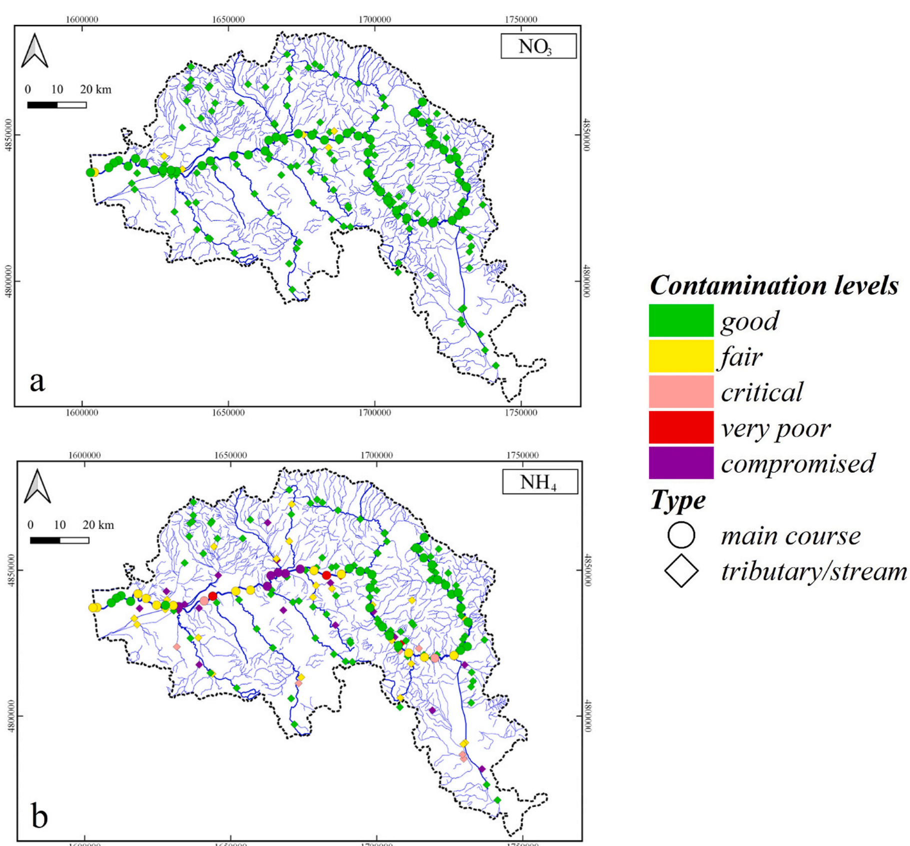

Fig. 4. Quality spatial trends in the Arno River Basin for (a) nitrate (NO_3) and (b) ammonium (NH_4). Contamination levels according to the ranking proposed in Chemeri et al. (2023) are reported in the legend.

associated with the highest values of chloride (Fig. 3c). The SO_4 scores in the ARB main catchment are low and therefore with a minimal impact on the river quality with the highest scores restricted to the terminal part of the river (Fig. 3d). High scores of sulphate are also found in the upper reaches of the Ambra river and in the final part of the Usciana channel as detected for both Cl and Na. Furthermore, the Elsa and Era tributaries are both characterized by a strong sulphate contamination with scores higher than 8 (Fig. 3d). While the high contents of Na and Cl detected in the Ombrone river and in the Usciana channel are associated with anthropogenic contributions (i.e., wastewater discharges) (Nisi et al., 2008a; Chemeri et al., 2026), the alarming levels of sulphate measured in the Elsa and Era rivers are, as previously mentioned, of geogenic origin and related to (i) the dissolution of gypsum-anhydrite formations (i.e., Burano and Gessoso-Solfifera formations, respectively) and (ii) discharge of thermo-mineral springs characterized by a Ca-SO_4 composition and with high salinity (Cortecci et al., 2002; Minissale, 2004; Nisi et al., 2008a, 2008b).

The spatial trends computed for the N-species (NO_3 and NH_4) are reported in Fig. 4. These compounds are recognized as major pollutants at global level and strictly regulated due to their adverse effects on both human and aquatic life (e.g., Schullehner et al., 2018; Blaisdell et al., 2019; Abascal et al., 2022; Taussi et al., 2024; Chemeri et al., 2026). In the ARB, NO_3 scores are extremely low, generally below 2 (Fig. 4a), as well as its relative impact on water quality (Chemeri et al., 2026). Contrarily, NH_4 shows critical contents in the Middle and Lower Valdarno (Fig. 4b) whereas in the upper reaches of the ARB, NH_4 scores are generally good. High contents in NH_4 are also found along some of the tributaries, specifically the Chiana, Era, Ombrone and Usciana rivers, and are likely related to "*fresh pollution*" associated with the discharge of waters deriving from zoo-technical, agricultural and tannery industries (Nisi et al., 2008a; Chemeri et al., 2026).

3.2. Temporal trends

The temporal trends were calculated for the Ombrone (T-Om), Usciana (T-Us) and Sieve (T-Si) tributaries of the Arno River and are represented in Fig. 5, while the full data are reported in the Supplementary Materials 1. In the computation, pH, EC, hardness, chloride, nitrate, sulphate, sodium and potassium were considered in the four available time frames according to Table 2.

The Ombrone and Usciana waters are characterized by a poor to extremely poor quality status (Fig. 5a–d) with Cl, Na and, secondarily, SO_4 as the main parameters influencing and compromising the CWQI values. It is worth mentioning that both tributaries exhibit unusually low CWQI values (corresponding to their minimum), indicating transient improvements in water quality, when sampled in T_{1b} (April 1989) and T_{3b} (May 2003) (Fig. 5a–c). These instances, however, represent exceptions when compared to the generally higher CWQI values observed throughout the various surveys. In particular, the notably low CWQI recorded in T_{1b} may be attributed to the high rainfalls that occurred in April 1989 (Fig. 5a–c) (Supplementary Material 2), which likely enhanced dilution processes and temporarily reduced pollutant concentrations in both rivers. In the Ombrone River, the CWQI values exceeding 4 are predominantly observed during periods of low

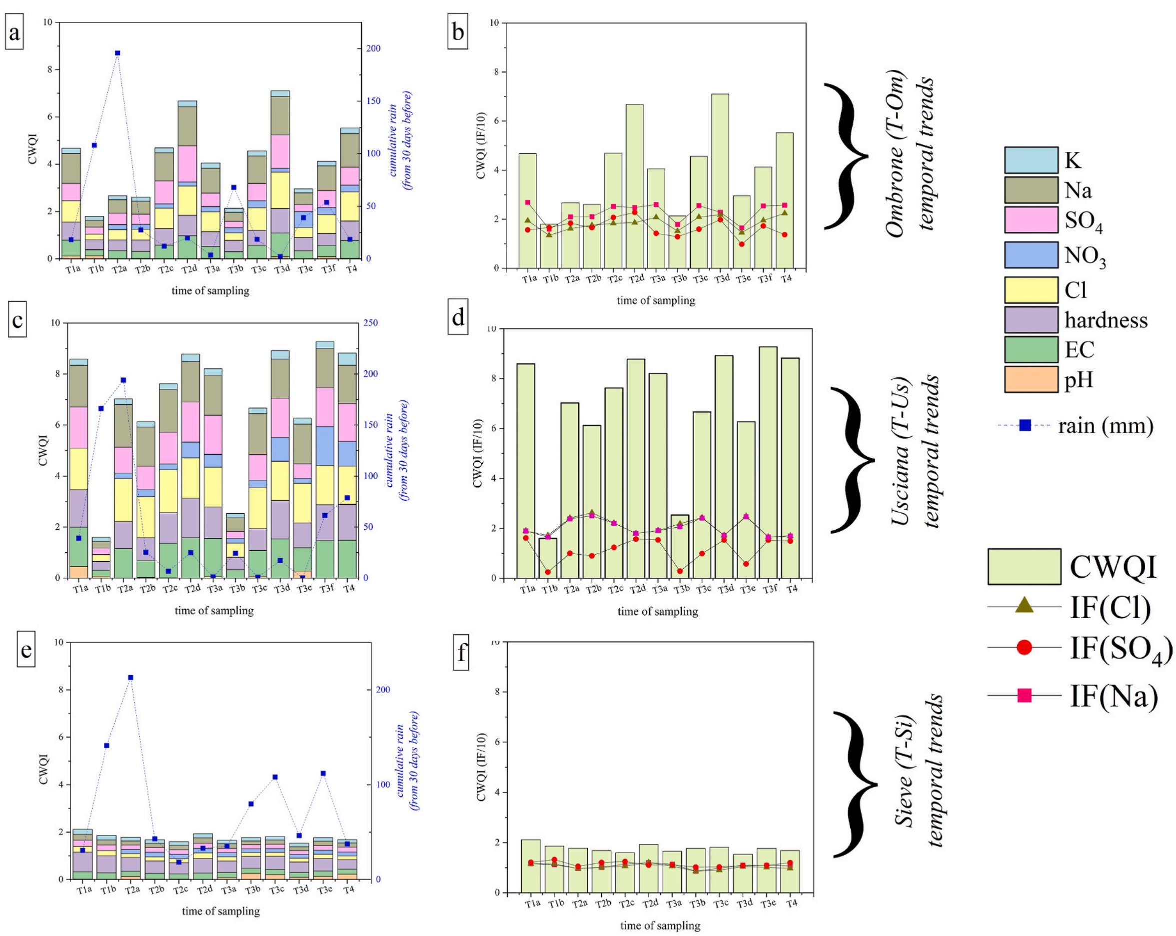

Fig. 5. Temporal trends calculated for the Ombrone (T-Om), Usciana (T-Us) and Sieve (T-Si) tributaries. The variation of the CWQI values over time are reported. In Figs. (a), (c) and (e), the relative contribution of each parameter to CWQI values is reported whereas in Figs. (b), (d) and (f), the influence factors (IF) for Cl, Na and SO_4 (calculated following eq. (4)) on the CWQI are reported. The influence is reported divided by ten (IF/10) for a better visualization. Full data are reported in the Supplementary Materials 1. Periods (T_1 to T_4) are reported according to Table 2a.

precipitation – namely at T_{1a}, T_{2c}, T_{3a}, T_{3c}, T_{3d}, T_4 (details reported in the Supplementary Material 2) –highlighting the significant role of seasonal variability and rainfall patterns in modulating water chemistry. Consequently, high CWQI values during drier periods suggest that limited rainfall leads to lower river discharge and reduced dilution capacity, thereby increasing the concentration of dissolved pollutants and degrading the overall water quality (Fig. 5a; Supplementary Material 1). Conversely, the influence of seasonality on the Usciana channel appears to be negligible (Fig. 5c), as no clear relationships emerges between the water quality status and the amount of precipitation recorded in the days preceding sampling. This limited responsiveness to rainfall variability may be attributed to the specific hydrological and geomorphological characteristics of the basin, as well as to the rate of pollutants released from anthropogenic activities persistently affecting the Usciana channel catchment (Nisi et al., 2008a, 2008b). In particular, the variability in pollutant release may also be linked to the type of anthropogenic contribution, as urban-industrial discharges are generally less influenced by precipitation, while agricultural and livestock effluents are more susceptible to rainfall, given their dependence on run-off and surface wash-off processes (e.g., Castiglioni et al., 2018; Guo and Chen, 2022). It is also important to highlight that, during the reference period (1990–2018), both the Ombrone and Usciana river basins experienced a significant increase in land use for anthropogenic purposes (Table 3). Specifically, the proportion of land in the Ombrone basin dedicated to human activities rose from 12.7 % in 1990 to ~17 % in 2018, representing a ~33 % increase. Notably, this value is more than twice the average anthropogenic land use observed across the broader ARB (5.1 % in 1990 and 6.9 % in 2018) (Table 3). Similarly, the Usciana catchment recorded an increase from 7.9 % to 10.7 % over the same period, marking a ~36 % growth and again exceeding the ARB average (Table 3). In parallel, both basins experienced a significant loss in land allocated to agricultural and forested uses. The Ombrone basin registered a 12.5 % decrease, while the Usciana basin showed a 7.7 % reduction, both surpassing the average land-use decline observed within the entire ARB (~4 %) (Table 3). These increasing percentages record a progressive transformation of the landscape, with natural and semi-natural land covers progressively replaced by urban and/or industrial developments. Such trends provide additional support for the observed lack of long-term improvement in water quality within the two river systems (Nisi et al., 2008a, 2008b).

Regarding the influence factors, in the Ombrone tributary (Fig. 5b), Na, Cl and SO_4 showed similar but highly variable IFs, likely related to the presence of multiple common sources related to complex interaction processes between anthropogenic and natural inputs, able to alter their concentrations. On the other hand in the Usciana channel, Na and Cl displayed the same pattern and contrarily, SO_4 shows a more variable and fluctuating behaviour (Fig. 5d), which may indicate a different source for SO_4 with respect to that of Na and Cl.

In contrast to the Ombrone and Usciana tributaries, the Sieve River did not exhibit significant variations in water quality across the four monitored time frames (Fig. 5e and f), consistently displaying CWQI values close to 2.00, which is indicative of good quality conditions. Furthermore, neither the relative-CWQI analysis nor the IFs assessment revealed the dominance of any specific parameter in driving the overall quality status (Supplementary Materials 1). These findings are consistent with previous studies (Cortecci et al., 2002; Nisi et al., 2008a, 2008b), which identified the Sieve River as a "*diluter*" of the Arno River, and together with the Pesa River (T-Pe), it ranks among the tributaries with the highest chemical quality and flow rates (Giani and Panichi, 2003). Notably, the primary contribution to the CWQI in the Sieve differs from that observed in the Usciana and Ombrone rivers, as it is mainly associated with water hardness. The latter reflects the geochemical setting of the basin, where water-rock interactions - specifically the rapid dissolution of carbonate minerals such as calcite and dolomite (Supplementary Material 3) - are the predominant processes influencing ionic composition (Chemeri et al., 2026). The geochemically driven signature, coupled with the absence of major urban or industrial pressures in the basin, suggests that the anthropogenic impact on the Sieve River is minimal or negligible (e.g., Cortecci et al., 2002; Nisi et al., 2008a; Chemeri et al., 2026). In fact, despite a noticeable increase over time, the share of land used for men-related activities remains less than half the average for the entire Arno basin (2.8 % vs. 6.9 %) (Table 3). Moreover, the loss of agricultural and forested lands in the Sieve catchment was minimal (~2.8 %) with respect to the Arno basin average (~4 %) and significantly lower when compared to the Ombrone and Usciana basins (Table 3).

3.3. Spatial-temporal trends

Eventually, the spatial-temporal trends were calculated for the sampling sites along the Arno River (AR-1 to AR-11) (Table 2b). The CWQI values were calculated taking into consideration the same

Table 4
Mean CWQI values and scores for Cl, SO_4 and Na in the Arno River waters. Samples' locations and temporal frames as reported in Table 2.

CWQI	T_1	T_2	T_3	T_4	score(Cl)	T_1	T_2	T_3	T_4
AR1	1.43	1.34	1.39	1.21	AR1	1.04	1.05	1.04	1.04
AR2	1.48	1.48	1.68	1.60	AR2	1.06	1.05	1.05	1.13
AR3	1.50	1.46	1.51	1.58	AR3	1.08	1.11	1.06	1.14
AR4	1.68	1.79	2.24	1.83	AR4	1.25	1.26	1.22	1.61
AR5	1.74	1.76	1.59	1.74	AR5	1.28	1.28	1.25	1.34
AR6	1.86	1.89	2.82	1.85	AR6	1.35	1.41	1.52	1.48
AR7	1.86	1.79	1.66	1.91	AR7	1.32	1.34	1.25	1.35
AR8	2.40	2.23	2.59	2.42	AR8	2.17	1.82	2.03	2.24
AR9	3.07	2.26	2.53	2.44	AR9	2.41	1.69	2.49	2.24
AR10	2.89	2.83	2.67	4.93	AR10	2.35	2.35	3.11	6.51
AR11	6.88	7.67	6.04	8.34	AR11	8.35	9.99	8.19	10.00
score(SO_4)	**T_1**	**T_2**	**T_3**	**T_4**	score(Na)	**T_1**	**T_2**	**T_3**	**T_4**
AR1	1.14	1.11	1.09	1.14	AR1	1.04	1.04	1.04	1.04
AR2	1.20	1.20	1.13	1.25	AR2	1.08	1.08	1.06	1.15
AR3	1.22	1.20	1.15	1.28	AR3	1.13	1.12	1.07	1.17
AR4	1.32	1.51	1.27	1.52	AR4	1.34	1.39	1.30	1.55
AR5	1.38	1.49	1.29	1.38	AR5	1.38	1.39	1.32	1.47
AR6	1.54	1.56	1.57	1.53	AR6	1.47	1.48	1.54	1.58
AR7	1.51	1.46	1.33	1.49	AR7	1.40	1.37	1.33	1.49
AR8	2.04	2.20	1.74	1.76	AR8	2.47	2.36	2.17	2.30
AR9	3.22	2.14	2.19	1.94	AR9	2.64	1.80	2.69	2.30
AR10	2.90	3.07	2.46	4.62	AR10	2.48	2.78	3.40	6.07
AR11	5.70	6.06	4.00	8.19	AR11	7.89	9.92	7.77	9.99

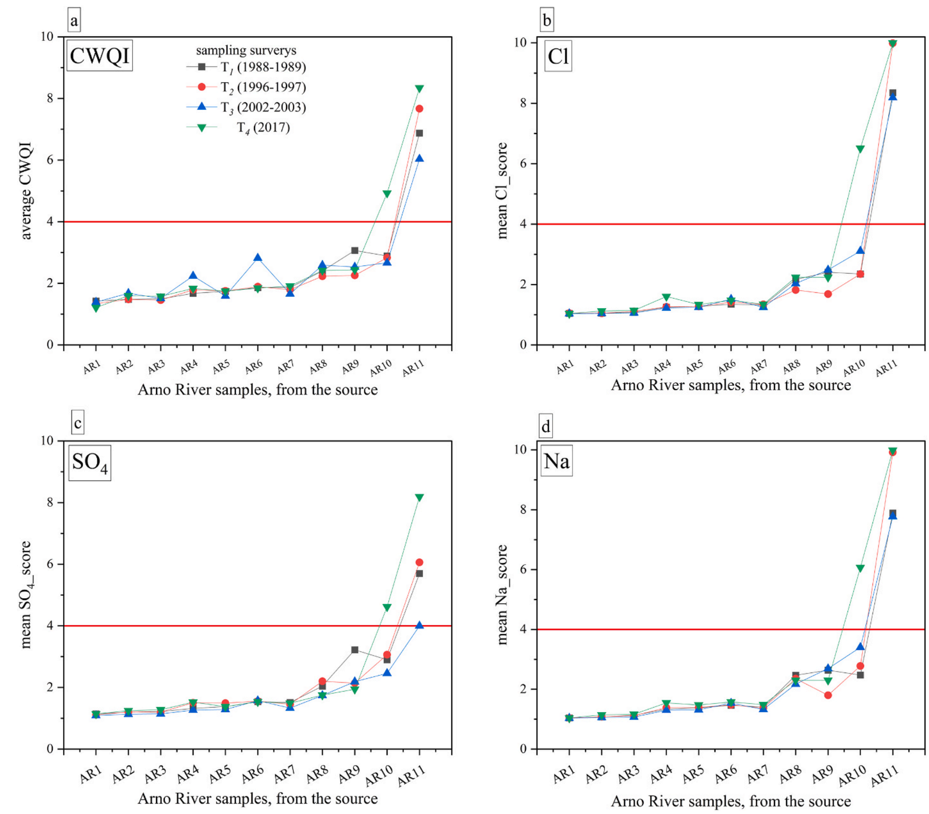

Fig. 6. Spatial-temporal trends for (a) CWQI, (b) chloride (Cl), (c) sulphate (SO_4) and (d) sodium (Na) calculated for the Arno River waters (AR1 to AR11, according to Table 2a). CWQI values are reported as the mean CWQI for the four-time frames while Cl, SO_4 and Na are reported as the mean score (s) for the four time frames, according to Table 2a). Data are reported in Table 4. Red horizontal line indicates the CWQI values (4.00) above which the water quality is considered poor or worse following Chemeri et al. (2023). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

parameters as for the tributaries in the previous sub-chapter. For an easier interpretation and a better visualization of the results, the CWQI computed data and scores ($s_{(Cl)}$, $s_{(SO4)}$ and $s_{(Na)}$) are reported as mean values for each time frame (Table 4; Fig. 6).

The CWQI values, similarly to the scores (Fig. 6; Table 4), display a trend in agreement with what shown in Fig. 3, with a good quality for those waters flowing upstream Florence, i.e., from AR-1 to AR-7 (Table 2), followed by a slight-to-strong quality deterioration as the Arno River meanders in the Middle and Lower Valdarno sub-basins, i.e., from AR-8 to AR-11 (Figs. 1 and 3). As previously discussed, the deterioration in quality reflects the increased anthropogenic load and influence along the main catchment. Furthermore, when the temporal aspect is considered, none of the sampling sites showed significant changes, suggesting that overall water quality conditions have remained relatively stable over the past three decades. However, some of the highest values for both the CWQI and the scores are referred to the last sampling survey carried out in 2017 (Chemeri et al., 2026). For example, both AR-10 and AR-11 had their peak values in 2017 with the former always being *fair* (CWQI<2.67 in T_3) and degrading to *poor* (4.93) in T_4 (Fig. 6a) following strong increases in the sodium, chloride, and secondarily, sulphate contents (Fig. 6b, c, d). Interestingly, sulphate concentrations at AR-08 and AR-09 show a slight but noticeable decrease during the last two sampling surveys (Table 4; Fig. 6b), which may tentatively suggest a positive response to environmental policies or improved wastewater treatment practices that have been implemented in recent years. However, this downward trend is abruptly reversed at the river mouth, where AR-10 and AR-11 display a substantial increase in SO_4 levels. In addition to sulphate, concentrations of sodium and chloride also rise sharply at these downstream sites (Fig. 6b–d). This general pattern likely reflects the combined influence of residual anthropogenic inputs and natural processes, particularly the contribution of marine intrusion to the Arno mouth zone. While the observed decline in sulphate upstream could likely be indicative of the partial effectiveness of environmental management measures, the dominant impact of saline intrusion in the downstream reaches appears to override these benefits. As a result, a marked deterioration of water quality is observed near the river outlet, where conditions remain significantly compromised. It should also be noted that the last survey (T_4) was performed in September 2017 following an unusually dry summer in Tuscany characterized by a low number of rainfall days (6) and reduced river discharge (Consorzio LaMMA, 2017). Such hydrological conditions likely enhanced the inland migration of the saltwater wedge, especially at AR-11, which is consistent with the Na and Cl sharp increases (Table 4; Fig. 6). At the same time, the reduced dilution capacity of the main catchment under low-flow regimes may have magnified the relative impact of local anthropogenic inputs, a process that is plausible at site AR-10, as it receives the heavily polluted waters of the Usciana channel (Fig. 1). At the latter site, water quality deterioration appears to result from the combined effect of local anthropogenic pressures and broader global change impacts, highlighting the dual contribution to the observed degradation.

These findings demonstrate that the water quality of the Arno River, as well as that of its tributaries, has remained nearly unchanged over the past 30 years, despite the implementation of various environmental regulations in recent years — such as the Water Framework Directive — aimed at reducing pollutant concentrations in aquatic systems. Furthermore, the same contaminated or *at-risk* areas, along with the same potential sources of pollution, continue to be identified (Bencini and Malesani, 1993; Cortecci et al., 2002, 2007; Nisi et al., 2008a, 2008b; Chemeri et al., 2026). This persistent pattern underscores the need for more effective environmental management strategies, particularly in consideration of the socio-economic significance of the Arno

River for the Tuscany Region. However, despite the fact that further plans are to be taken for ameliorating the ARB quality, the increasing anthropogenic stress in the last decades on the ARB did not produce a worsening of the surface waters, suggesting that the undertaken environmental actions were able to, at least partly, moderate/minimize the human pressure. From a management perspective, the CWQI (and the presented approach) represents a practical tool to translate complex geochemical data into clear and comparable values that can guide decision-making. By highlighting contamination hotspots and areas possibly vulnerable to pollution, it allows managers and environmental agencies to prioritize mitigation actions and allocate resources more efficiently. Furthermore, the approach can be applied repeatedly to evaluate the effectiveness of environmental regulations, as demonstrated by the relative stability of the Arno River Basin despite rising anthropogenic pressures. Thanks to its simplicity and adaptability, the CWQI is suitable for integration into monitoring programs, supporting communication between scientists, policymakers, and stakeholders, and enabling adaptive water management strategies.

4. Conclusion

This study described a simple and operationally efficient methodological framework for evaluating surface water quality using the Chemical Water Quality Index (CWQI) (Chemeri et al., 2023). The approach has proven to be easily applicable, flexible, and capable of tracking both spatial and temporal quality trends, thus offering a practical tool for assessing the geochemical evolution of river systems. By combining spatial, temporal, and spatial–temporal perspectives, CWQI-based analyses allow for the identification of contamination hotspots, the quantification of the relative influence of different solutes, and the evaluation of long-term water quality dynamics in relation to environmental changes and management practices. Its operational nature makes it suitable for the streamlined processing of large datasets and for providing decision-support insights to environmental agencies, monitoring programs, and water managers. In particular, CWQI enables the identification of high-risk areas, the prioritization of mitigation measures, and the monitoring of the effectiveness of regulatory frameworks or remediation actions. In this sense, the strength of our work lies not only in the case study results, but also in the novelty of the integrated CWQI-based framework itself, which provides a creative yet operational way to interpret complex geochemical datasets and extract management-relevant insights.

Future developments of this methodology could further enhance its potential. Expanding the number of regulated parameters would provide a more comprehensive picture of water quality, while denser temporal datasets would improve the ability to distinguish seasonal fluctuations, long-term climatic trends, and anthropogenic impacts. Some methodological limitations should be acknowledged, including potential data gaps and the absence of biological parameters, which could be integrated into the CWQI computation to better assess ecosystem health. Concrete next steps include combining CWQI with biological and ecotoxicological indices, extending spatial and temporal coverage, and testing the approach in additional river basins with diverse hydrogeological and climatic contexts. Collectively, these improvements will also enhance our understanding of underlying processes and enable the identification of the main drivers and forcing factors controlling water composition. These refinements would strengthen the methodology and offer deeper insights into river ecosystem functioning, supporting more integrated and sustainable water resource management.

CRediT authorship contribution statement

Lorenzo Chemeri: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Marco Taussi:** Writing – review & editing, Validation, Investigation, Conceptualization. **Jacopo Cabassi:** Writing – review & editing, Investigation, Conceptualization. **Barbara Nisi:** Writing – review & editing, Formal analysis. **Orlando Vaselli:** Writing – review & editing, Formal analysis. **Stefania Venturi:** Writing – review & editing, Validation, Supervision, Methodology, Investigation, Conceptualization.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2025.123149.

Data availability

Data will be made available on request.

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