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TITOLO DELLA TESI

"Advancements in Agricultural Sustainability Through Precision Farming and Wastewater Reuse: a Comprehensive Study on Intelligent Resource Management in Rural Development"

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Ciclo XXXVI

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Introduction

Smart management of productive inputs. Why Precision Agriculture?

Precision agriculture (PA) is positioned between of agronomic science and technological innovation, aiming to optimize the efficiency and sustainability of agricultural practices. The European Commission's focus on innovation and sustainability in agricultural production, as promoted by the new post-2020 Common Agricultural Policy (CAP), emphasizes the importance of effective nutrient management. The need for the sustainable intensification of agriculture, which seeks to increase food production while minimizing environmental impact, sets the critical context for this research. Therefore, this PhD work initially focuses on optimal nutrient management, with a particular emphasis on nitrogen (N) use efficiency. This choice is motivated by several factors: nitrogen is recognized as a crucial limiting element for crop productivity, especially in cereals. Inadequate nitrogen management can lead to reduced yields, decreased soil fertility, and negative environmental impacts (Passioura, 2002). Despite the extensive use of nitrogen fertilizers, a significant proportion is not absorbed by crops, leading to pollution and health risks. Thus, improving nitrogen use efficiency (NUE) by optimizing application timing and dosages is crucial to making the system more efficient (Hawkesford, 2014; Denora et al., 2022). In this context, precision agriculture represents a promising solution to overcome these challenges. By employing variable rate technology (VRT) and spatial management, along with balanced nutrient dosing adapted to actual crop conditions and possibly exploiting vegetation indices, PA allows for a more targeted and efficient use of nitrogen. This approach not only addresses the spatial variability of nitrogen in the soil but also supports the creation of homogeneous management zones for differentiated optimization, improving both agronomic and economic outcomes (Denora et al., 2023). The exploration of management zones through geophysical soil mapping and the use of clustering algorithms demonstrates the sophistication of PA techniques in identifying the inherent variability of agricultural soils (Castrignanò et al., 2018). In this perspective, we sought to validate and implement such methodologies, particularly the k-means algorithm, to create high-quality prescription maps for precision agriculture. This PhD work aims to contribute to the knowledge and dissemination in real environments of PA techniques to improve nutrient management, crop productivity, and environmental sustainability. It aims to provide a comprehensive view and application of PA techniques with a particular focus on durum wheat production in the Mediterranean context.

Water Resource Management: Why Reuse Wastewater in Agriculture? Risks or Benefits?!

The global agricultural sector faces a critical challenge, as it consumes 70% of the world's freshwater resources, a figure that increases in developing countries. The looming threat of water scarcity in agriculture is expected to affect over 80% of cultivated lands globally, exacerbated by the dual pressures of population growth and climate change (Liu et al., 2022; Rosa, 2022). This scenario places irrigation management at the forefront of agricultural sustainability, particularly in water-stressed regions, where the implications of climate change and water scarcity concern the economy, cropping patterns, production, food demand, and consumption (Verlicchi et al., 2023) The growing use of treated wastewater, or reclaimed water, as a source of sustainable irrigation represents a paradigm shift to address these challenges (Ungureanu et al., 2020). Particularly, the Mediterranean basin, characterized by arid and semi-arid conditions, has been a pioneer in using treated wastewater in agriculture, contributing to 5-12% of the total treated wastewater (Hashem and Qi, 2021) . This practice not only promises greater agricultural profitability and reduced dependence on synthetic fertilizers, thanks to the nutrient-rich nature of the recovered water, but also contributes to the conservation of diminishing freshwater resources. However, the adoption of wastewater irrigation introduces a complex set of challenges, including concerns about soil salinity, risks of pathogens and heavy metals, and socioeconomic factors. Of particular concern are the environmental impacts posed by emerging contaminants (ECs) - a heterogeneous group of unregulated chemicals detected in various environmental matrices, with potential human and ecological exposure (Rout et al., 2021). The motivations behind our doctoral work on wastewater reuse are focused on the urgent need to address these challenges. By studying the presence, fate, and impact of pharmaceuticals and other ECs in crops irrigated with treated wastewater, we aim to provide critical insights into sustainable agricultural practices. This study, focused on the Mediterranean context, specifically examines the levels of ECs in tomato plants (*Solanum lycopersicum* L.) and durum wheat (*Triticum durum* Desf.) grown under treated wastewater irrigation conditions in Southern Italy, using lysimeters to mimic real-world agricultural contexts (Mishra et al., 2023). Our research is driven by the broader implications of water scarcity, the potential of treated wastewater as a source of sustainable irrigation, and the critical need to understand and mitigate the risks associated with ECs in agriculture. It seeks to contribute to the development of safe, effective, and environmentally respectful irrigation practices that can support the dual goal of water conservation and sustainable food production.

Considering the challenges posed by emerging contaminants, the study emphasizes the importance of interdisciplinary approaches, combining agronomic and chemical-analytical expertise to advance our understanding of water reuse in agriculture. Exploring the distribution and impact of pharmaceutical products in the soil-plant-atmosphere context. This initiative not only aligns with global efforts to improve agricultural sustainability but also contributes to the growing knowledge of the safe and effective use of unconventional water resources in agriculture. Through this work, we aspire to inform future policy, practice, and research on wastewater reuse.

Purpose of the PhD

This doctoral work aims to optimize crop yield and quality through precision agriculture methodologies and to promote a sustainable agricultural model that includes the conscious and safe reuse of water resources, in line with a circular and responsible approach with the singular goal of resource management in such a complex historical period. This work was made possible thanks to several regional and national projects (Rural Development Program of Basilicata Region - mis. 16.1; 16.2, PRIN) which have allowed us to be a bridge between the world of research and experimentation and the real agricultural context with its daily environmental and socio-political challenges. The doctoral program intends to impact the real-world context by improving resource use within the agricultural setting of southern Italy. To achieve this goal, the doctoral activities have been organized as follows:

- **Chapter 1: Geophysical Field Zoning for Nitrogen Fertilization in Durum Wheat (*Triticum durum* Desf.)**

  Objective: To implement variable rate technology (VRT) for nitrogen fertilization in durum wheat cultivation, integrating soil property maps from electromagnetic measurements to enhance yield quality and environmental sustainability.

  Result: The application of VRT led to a 25% reduction in nitrogen fertilizer use while maintaining yield levels compared to uniform application. VRT also resulted in higher grain protein content and nitrogen use efficiency, indicating reduced environmental impact and enhanced economic profitability.

- **Chapter 2: Validation of Rapid and Low-Cost Approach for the Delineation of Zone Management Based on Machine Learning Algorithms**

  Objective: To validate a machine learning-based approach for delineating management zones in durum wheat fields using electromagnetic induction maps, aiming at improving soil management and crop yield.

  Result: The k-means algorithm successfully identified management zones with significant differences in soil characteristics and crop response, validated agronomically by improvements in yield and soil health. UAV-derived vegetation indexes correlated with soil properties, suggesting the importance of timing in multispectral image acquisition.

- **Chapter 3: Precision Nitrogen Management in Rainfed Durum Wheat Cultivation: Exploring Synergies and Trade-offs via Energy Analysis, Life Cycle Assessment, and Monetization**

Objective: To evaluate the environmental, energetic, and economic impacts of precision nitrogen management using VRT compared to uniform applications in durum wheat production.

Result: VRT improved energy use efficiency, reduced environmental impacts, and offered indirect economic benefits. The multi-indicator model highlighted the potential of VRT for sustainable agriculture, emphasizing the importance of employing multiple metrics for comprehensive sustainability assessment.

- **Chapter 4: Uptake and Accumulation of Emerging Contaminants in Processing Tomato Irrigated with Tertiary Treated Wastewater Effluent: A Pilot-Scale Study**

  Objective: To investigate the uptake, accumulation, and translocation of emerging contaminants in tomato plants irrigated with treated wastewater, assessing potential risks to food safety and environmental health.

  Result: Significant differences in the behaviour and distribution of ECs were observed between different irrigation strategies, with some contaminants showing active uptake by plants. This raises concerns about the introduction of ECs into the food chain and their implications for human health and the environment.

- **Chapter 5: Fate of Emerging Contaminants in Durum Wheat: Perspectives for Food Safety and Agricultural Sustainability**

  Objective: To assess the presence and distribution of emerging contaminants in durum wheat crops irrigated with treated wastewater, evaluating implications for food safety and agricultural sustainability.

  Result: The study identified significant accumulations of certain pharmaceuticals in durum wheat, highlighting the complex behaviour of ECs in agricultural settings and the need for careful risk assessment and guidelines for treated wastewater use in irrigation.

This PhD work contributes significantly to the fields of agronomy and sustainable agriculture by providing innovative solutions for precision farming, environmental protection, and the safe reuse of resources, thus supporting the advancement of agricultural practices towards greater sustainability and efficiency.

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Chapter 1. Geophysical field zoning for nitrogen fertilization in durum wheat (Triticum durum Desf.*)*

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Abstract

The current social context requires an increase in food production, improvement of its quality characteristics and greater environmental sustainability in the management of agricultural systems. Technological innovation plays a great role in making agriculture more efficient and sustainable. One of the main aims of precision farming (PF) is optimizing yield and its quality, while minimizing environmental impacts and improving the efficient use of resources. Variable rate techniques (VRT) are amongst the main management options for PF, and they require spatial information. This work incorporates maps of soil properties from low induction electromagnetic measurements into nitrogen (N) balance calculations for a field application of VRT nitrogen fertilization of (*Triticum durum* Desf., var. Tirex). The trial was conducted in 2018–19 at Genzano di Lucania (PZ, Italy) geologically located on the clayey hillsides of the Bradanica pit and the Sant'Arcangelo basin. Three soil homogeneous areas were detected through low induction electromagnetic measurements and used as uniform management zones. The amount of nitrogen fertilizer to be applied by VRT was calculated on the base of estimated crop nitrogen uptake and soil characteristics of each homogeneous area. Crop response to VRT was compared to uniform nitrogen application (UA) on the whole field. The application of VRT resulted in a reduction of 25% nitrogen fertilizer with the same level of yield respect to UA. Grain protein content, as well as gluten content and N content, were significantly higher in VRT than in UA. As a consequence of lower nitrogen input and higher levels of N removal, VRT reached a higher nitrogen use efficiency than UA, and this indicates a lower environmental impact and a higher economic profitability.

Introduction

Effective nutrient management is key for future challenges linked to sustainable development. Specific issues include avoiding environmental losses and preserving or improving yield and quality of crops [1, 2]. Nitrogen is one of the main constraints limiting crop yield [3], especially for cereals where low nitrogen or poor nitrogen management reduce yield, residual soil fertility, quality, and environmental sustainability [4, 5]. However, the massive use of N fertilizers is harmful for terrestrial and water ecosystems, air pollution as well as human health [6], with only 33% actually used by plants [7]. Nitrogen use efficiency (NUE) is the fraction of applied nitrogen that is taken up and used by crops, therefore increasing NUE by optimizing times and rates of application is crucial for improving sustainable and productive agriculture [4].

Optimizing N may be pursued through timing and choosing stabilized forms of N [8] or through spatial management [9, 10], or precision dosing based on crop vegetation indices [11]. Different level of soil N mineralization, leaching, volatilization, and crop uptake, generate a spatial variability of N in the soil, justifying the application of variable rate techniques (VRT) to N fertilization [12]. Durum wheat is a staple in the Mediterranean area where traditional uniform within-field management results in low time and space efficiency [13]. Precision farming (PF) supported by the use of different technologies [14–16] is an important approach to address nitrogen efficiency through differential management in space.

Criteria for fertilizing different zones in the same field vary, and the debate as to whether lower-yielding field regions should be fertilized with lower or higher rates of N is still under research [17] and the analysis implies agronomic and economic issues [18].

A classical problem in PF is the definition of uniform management zones, i.e., field regions within which agronomic practices should be applied uniformly, and different enough from other regions that management should differ between them. Earlier approaches were based on the analysis of time-series of data on crop behaviour, such as multi-year yield maps or vegetation indices [9]. Geophysical mapping of soil properties has proved capable of detecting soil features related to crop behaviour [11, 19] and more specifically to wheat yield and quality [20] and has thereafter been used to delineate uniform management zones [21]. Criteria for incorporating geophysical mapping in PF management range from using geophysical data alone [22], to coupling them with other properties of fields and crops. The coupling of soil data and crop yield was used by Guerrero et al. [17] to compare N fertilization strategies in barley and wheat. The joint analysis of geophysical soil maps and plant properties implies the need of addressing complex features of different spatial datasets with measures that are repeated in time [23, 24]. Overall, field zoning for PF is based on spatial data, but new principles of PF need to be combined with well-defined principles of plant nutrition, soil chemistry and chemistry of the fertilizer elements. Nitrogen balance is a classical agronomic fertilization criterion based on predictions of nitrogen uptake considering the actually obtainable yield; corrections are then applied for soil nitrogen content and interactions between the fertilizer and the main physical and chemical soil parameters [25].

This work aims to use geophysical soil mapping coupled with differential nitrogen balance as a basis for the rapid delimitation of uniform management zones for the application of variable rate nitrogen fertilization in durum wheat.

Materials and methods

Field trials

The trial was conducted in 2018–19 at Genzano di Lucania (PZ) latitude: 40.82° N, longitude: 16.08° N. The study area (4,07 ha^{-1}) is located on the clayey hills of the Bradanica grave and the basin of Sant'Arcangelo (Fig 1). The soil spatial variability was detected by mean of low induction electromagnetic technique with a Miniexplorer (GF Instruments Brno-CZ) (Fig 2A) detecting bulk soil electrical conductivity (Cb) at three depths (0–50 cm, 0–100 cm and 0–180 cm-. The survey was conducted with a distance of 6 m between transects and average measurement distance of 0.8 m along transects (Fig 2B) and Cb values were converted to Electrical resitivity Rho = 1/Cb (Ohm m). Three electrical resistivity maps were obtained (Fig 3) [17, 18], and values of resistivity were averaged over the three depths. The field was divided in three zones according to the following average values: zone 1: 23.03 Ohm m, zone 2: 12.81 Ohm m and zone 3: 18.29 Ohm m. The coefficient of variation of resistivity values within each zone was: zone 1: 13%, zone 2: 12%, zone 3: 11%. The surface areas of the three zones were: area 1: 0.29 ha^{-1}; area 2: 1.9 ha^{-1}; area 3: 1.88 ha^{-1}.

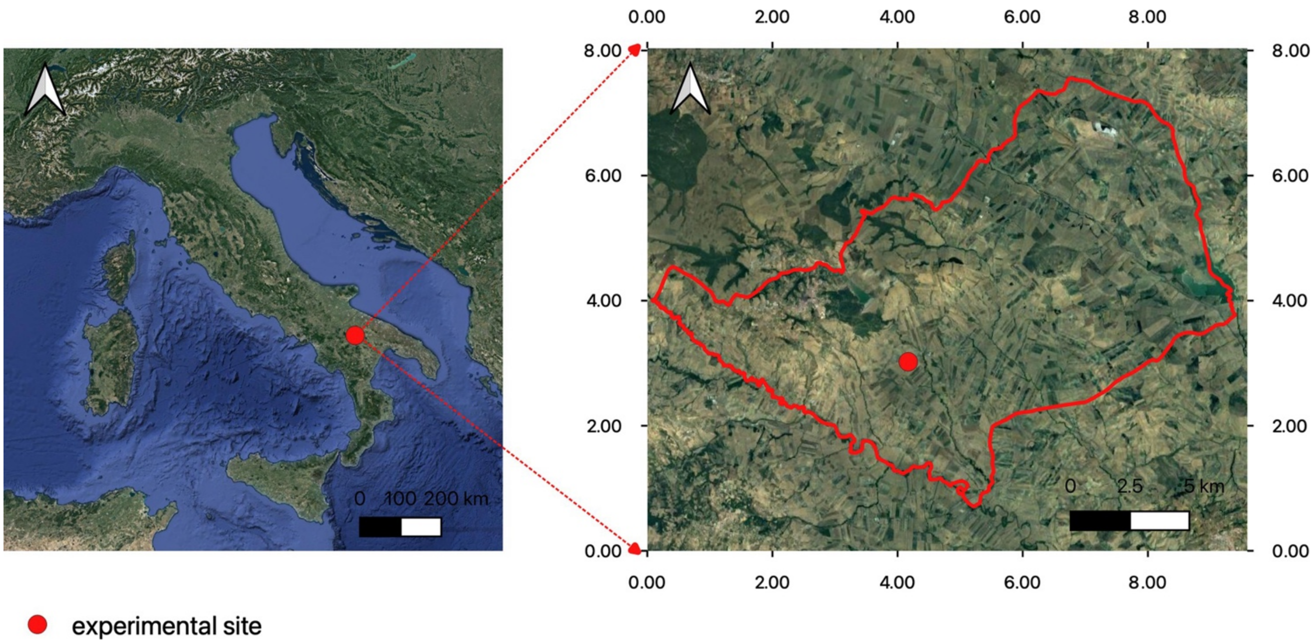

Fig 1. *Location of experimental site.*

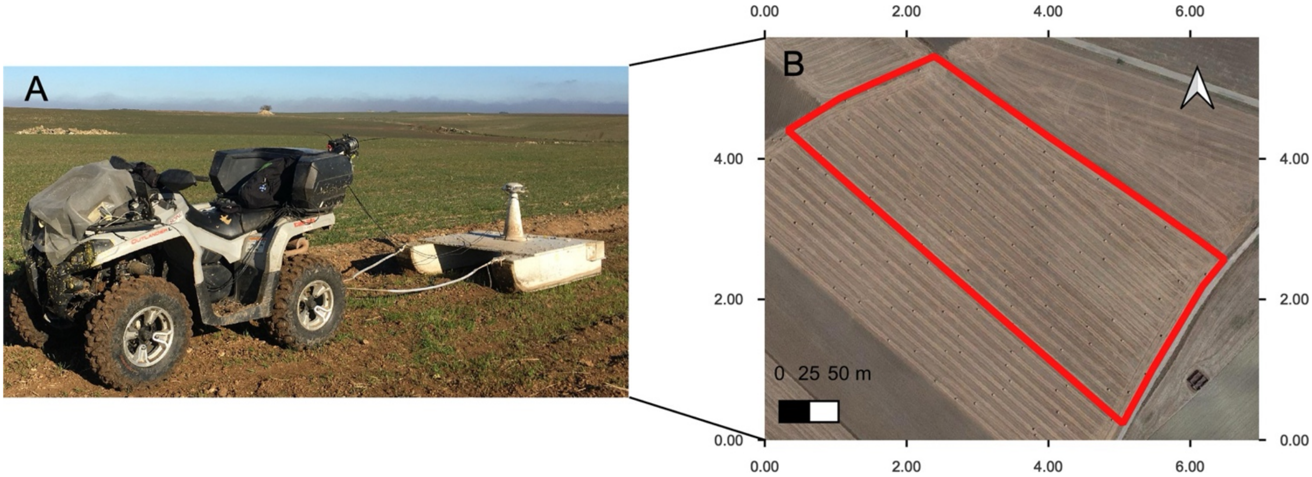

Fig 2. *Soil spatial variability with electromagnetic induction technique. Low induction electromagnetic soil mapping (A, B), miniexplorer, GF Instruments (A), area tested by the instrument (B).*

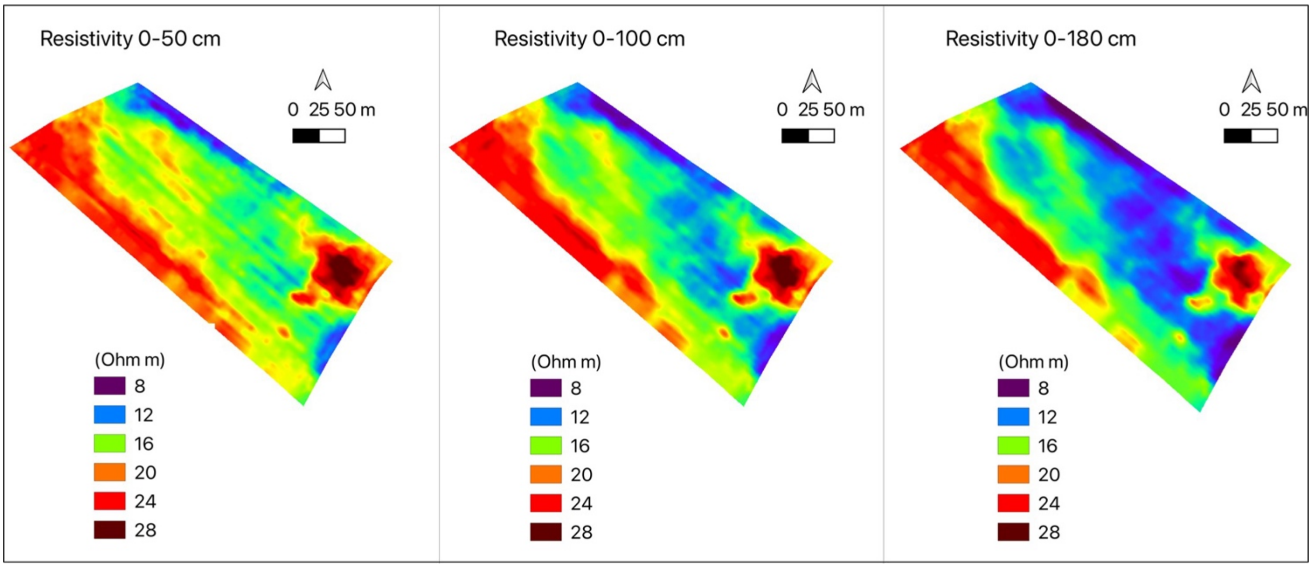

Fig 3. *Resistivity maps of experimental field.*

Across the whole field durum wheat (*Triticum durum L.*, var. Tirex) was sown with inter row spacing of 0,13 m and 250 kg ha^{-1} of seeds were used. Soil tillage consisted in a 40 cm deep plowing (August 28, 2018) and two harrowing (November 11 2018 and December 5 2018) with seeding (December 18 2018). A pre-sowing fertilization was broadcast applied with 92 kg ha^{-1} of P_2O_5 and 36 kg ha^{-1} of N. We tested the hypothesis that variable-rate fertilization is more efficient than uniform application by comparing two N fertilization strategies: variable rate (VRT) and uniform (UA) on three replications in each of the areas identified through soil mapping. The amount of N fertilizer to be applied was calculated based on estimated crop N uptake and soil characteristics of each homogeneous area as follows: crop potential N uptake was estimated based on the crop yield of previous year in each homogeneous area and was corrected considering the N contribution provided to the crop by the mineralization of the organic matter. N mineralization was calculated considering the content of organic matter in the soil profile explored by the roots, its content in organic N and by the mineralization efficiency which in turn depends on the car- bon/nitrogen ratio of the soil (1 for C/N < 9; 0,5 for C/N >9, C/N<12). For the VRT treatment, the N doses applied in each area through a variable rate spreader are reported in Table 1. A dose of 35 kg ha^{-1} of N (UREA 46%) was spread in pre-sowing over the entire field. At the phenological stage of end tillering, a different rate according to the soil spatial variability was spread in each area at the end of tillering (Table 1). For each treatment we established

Table 1. Units of N supplied in the different experimental zones.

Distribution mode	Zone	Dose of N (kg ha^{-1}) pre-sowing	Dose of N (kg ha^{-1}) end tillering	N_{tot} (kg ha^{-1})
Uniform (UA)	1	35	85	120
	2			
	3			
Variable Rate (VRT)	1	35	121	156
	2	35	63	98
	3	35	36	71

plots of 2x2 m^2 replicated three times inside each of the homogeneous areas identified in the field. In all such plots we applied a dose of N equal to 85 kg/ha (UA), which corresponds to the amount generally applied by the farmer, and slightly over the average of the dose of N applied in the three zones. The fertilizer was manually spread in UA.

Soil analysis

Following the soil spatial variability determined by electrical resistivity, in each of the identified homogeneous areas, soil samples were collected at regular grid intervals in triplicate after the harvest at the depths of 0–40 cm and characterized by conventional analytical methods according to Page et al. [26]. All samples were airdried and 2-mm sieved before laboratory analyses. Particle size distribution was determined by the pipette method after removing carbonates and organic matter and the textural class of the soil was identified by the USDA soil textural classification system [27]. The organic carbon (OC) content was measured by the Walkley-Black method, and the total Kjeldahl N was determined by the Kjeldahl method. The available phosphorus (Pava) was determined by ultraviolet and visible (UV–vis) spectrophotometry according to Olsen method [26]. The total content of $CaCO_3$ was determined by the gas-volumetric methods (Dietrich–Freuling calcimeter method), whereas the active lime was extracted with 0.1 M ammonium oxalate and determined by titration with 0.1 M $KMnO_4$. In Table 2, the main physico-chemical characteristics for the computation of N fertilization are reported.

Biomass yield and grain quality

At the harvest, plant samples on 1 linear meter were taken. Dry biomass weights were determined multiplying the fresh weights by the percentage of dry weight obtained by drying samples at 70°C to constant weight. At harvest, was measured yield and its components (n ears/m^2, n seeds/ear, total yield) and grain qualitative parameters (protein con- tent, specific weight, gluten and yellow index with a FOSS Infratec 1241). On grain and straw, the N content was measured using a TOC analyzer (soli TOC1 cube, Elementar, Hanau, Germany). Nitrogen use efficiency (NUE) was calculated as the ratio between total N uptake (calculated by multiplying the N concentration for dry biomass) by the crop of each experimental treatment and N applied with fertilizer [28].

Table 2: *Main soil physico-chemical characteristics of the three experimental zones*.

Soil Proprieties	Zone 1	Zone 2	Zone 3
Sand 2.0–0.05 mm (%)	56	27	32
Silt 0.05–0.002 mm (%)	25	32	31
Clay $<$ 0.002 mm (%)	19	41	37
Soil texture (USDA)	Sandy Loam	Clay	Clay Loam
Total N (g/kg)	0.4	1.1	1.2
Available phosphorus (P mg/kg)	6.0	7.0	10.0
Exchangeable potassium (meq/100g)	0.3	1.1	1.0
Organic matter (%)	0.5	1.9	2.2
Organic carbon (%)	0.3	1.3	1.1
C/N ratio	7.9	9.4	10.2
Cation Exchange Capacity (meq/100g)	14.6	24.6	24.7
pH	8.3	8.2	8.1
Aptitude for wheat cultivation	marginal	sub-optimal	sub-optimal

Statistical analysis

The dataset was analyzed using “the lme4 package” of the “R” statistical software, version 3.6.3 [29]. After testing the basic assumptions of analysis of variance (ANOVA) as the normal distribution of the experimental error by Shapiro-Wilk’s test together and the homoscedasticity by means of the Levene test, the ANOVA model was performed. A split–plot design with three replicates considering zone, N fertilization (UA, VRT), zone x N fertilization has been used. All the factors were considered as fixed, while the replicates as random. The statistical significance of the difference among the means was determined using Tukey’s honest significance difference post hoc test at the 5% probability level.

Results

Weather conditions

Temperature and precipitation recorded during the wheat growing period (October 2018 to June 2019) are reported in Fig 4. Heavy rainfall occurred in the period October-December 2018 (171.20 mm from 1/10 to 17/12), and this caused sowing on wet soil. Soil compaction due to wet conditions, resulted in a reduced emergence, and therefore a low density of plants and ears, particularly on the clay soil of zone 2.

January to February, were characterized by high temperature, with maximum temperatures reaching 20°C (Fig 4). From mid-April, the rains were prolonged and of strong intensity,

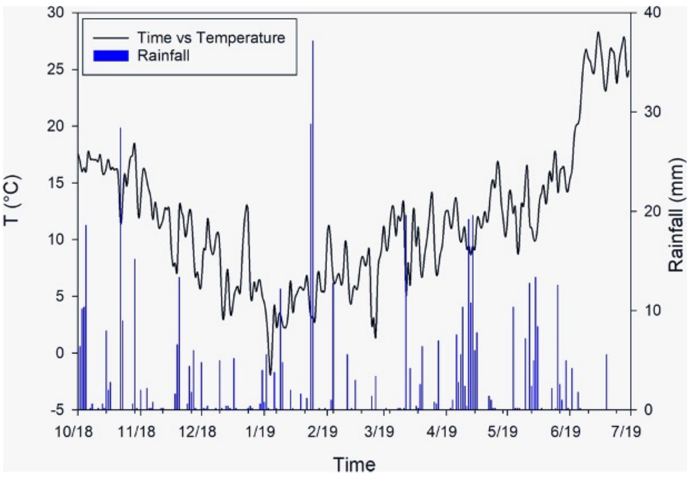

Fig 4. *Weather conditions. Monthly average precipitation and temperature during the study period of winter wheat growing cycle (October 2018 to June 2019).*

exposing the crop to potential damage during the delicate phase of earing. The end of the vegetative cycle took place with high temperatures and almost total absence of precipitation.

Yield response

The total biomass and grain yield of zone 2 was significantly lower respect to that of both zones 1 and 3 (Table 3). Regarding straw yield, differences were significant between zones 2 and 3 only, whereas the number of ears m^{-2} was significantly different between all zones.

A significant relationship was found between the density of ears and grain yield across zones (Fig 5). No significant differences were detected between UA and VRT for yield parameters, in spite of different amounts of N applied with the two treatments. Also, interaction of zone and N application method were not significant except for density of ears in zone 2 only, where differential application of N resulted in a significantly higher number of ears m^{-2} (Table 3).

Grain quality and nitrogen use efficiency

The qualitative grain traits measured at harvest are reported in Table 4. Zone 1 showed a significantly higher content of grain protein, yellow colour, gluten, and N compared to both zones 2 and 3. N uptake calculated on the basis of total straw + grain removal was lowest in Zone 2, whereas NUE showed a significant interaction between zone and distribution mode, since only in zone 3 the VRT is more efficient than UA. (1.68 vs 0.92). On the contrary, in positions 1 and 2 no significant differences were observed between UA and VRT in terms of NUE. Nevertheless, VRT in zone 3 is more efficient than all other treatments and UA in zone 1 and 3 is also more efficient than UA in zone 2.

Grain protein and gluten were significantly higher in VRT, whereas the superiority of VRT in grain nitrogen percent and total uptake was not statistically significant. The value of nitrogen use efficiency in VRT across field zones was equal to 1.03, significantly higher than that of 0.78 in UA.

Discussion

Data from this experiment show that areas chosen on the basis of soil resistivity mapping within a field corresponded to different soil textures and crop behaviour. In particular zone 2,

Table 3. *Biomass and yield in the different experimental conditions of durum wheat.*

Treatment	Total biomass (t ha^{-1})	Grain yield (t ha^{-1})	Straw yield (t ha^{-1})	ears m^{-2}
Zone 1	9.2 a	3.0 a	6.1 ab	247 b
Zone 2	6.5 b	1.7 b	4.8 b	221 c
Zone 3	10.8 a	3.2 a	7.5 a	282 a
Significance	***	***	**	*
Zone 1 x UA	9.1	3.1	6.1	244 ab
Zone 1 x VRT	9.2	2.9	6.2	251 ab
Zone 2 x UA	6.3	1.7	4.6	200 c
Zone 2 x VRT	6.7	1.8	4.9	241 ab
Zone 3 x UA	10.7	3.2	7.4	308 a
Zone 3 x VRT	10.9	3.2	7.6	256 ab
Significance	n.s	n.s.	n.s	*

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' Significance at P<0.05; **, significance at P< 0.01; ns, no significant difference. Different letters indicate significant different.

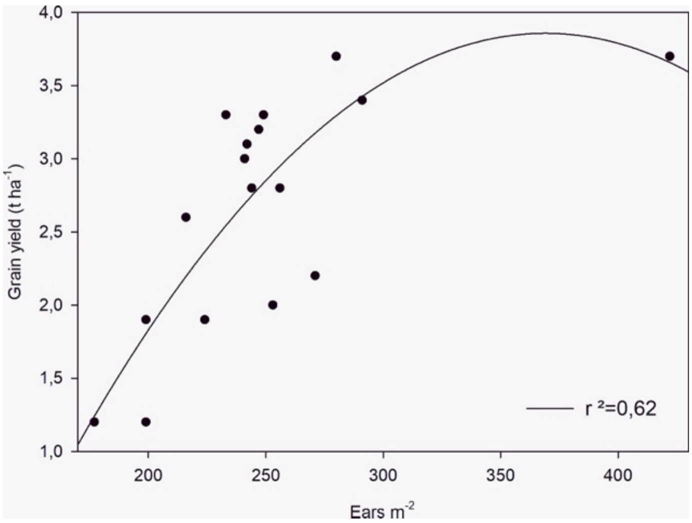

Fig 5. *Relationship between yield and number of ears measured in the experimental conditions.*

characterized by clayey texture, showed lowest biomass, yield and nitrogen uptake, while zone the sandy-loam area (zone 1) had highest grain quality. Overall nitrogen use efficiency was highest in zone 3, a clay loam area within the field. The low yield in area 2 may be ascribed to the high content of clay and the consequent risk of waterlogging and poor tolerance of machine traffic in case of high precipitation during crucial times such as sowing. This interpretation is supported by the lower number of ears reported in Table 3 for this field region. Such constraints due to soil physical properties were therefore more effective in determining yield than the more favourable soil chemical characteristics of shown in Table 2. This is confirmed by the significant relationship we found between the density of ears and grain yield across zones in our field (Fig 5). This also means, that the computation of N supply based only on the soil characteristics is not sufficient. For an accurate computation of N supply by VRT techniques, the real crop conditions at the moment of fertilizations have to be considered. In accordance with Song et al. [30] soil characteristics should be combined with crop remote sensing for a more accurate computation of site-specific N fertilization.

In our data no significant differences were detected between UA and VRT for yield parameters, in spite of different amounts of N applied with the two treatments. This result could be ascribed to no changes in soil chemical parameters after the use of different doses of N fertilization [31, 32]. Also, interaction of zone and N application method were not significant except for density of ears in zone 2 only, where differential application of N resulted in a significantly higher number of ears m^2 (Table 3). Therefore, N was able to compensate for the negative effects of a high clay content on plant density on the production of ears, which was correlated with yield.

Overall, results can be commented by saying that soil conditions dominated over N application in determining yield, and therefore the choice of N treatments needs to be made exclusively in terms of savings in N fertilizer, rather than in potential increases in yield. In the whole 4.07 ha^{-1} field the application of precision farming, gave as a result a reduction of 25% of N application in VRT respect to UA (373 Kg in VRT and 498 in UA Kg of N in 4,07 ha^{-1}).

Although our data come from one year only, they confirm that if VRT is applied to N fertilization, the computation of N fertilizer rate considering only physico-chemical characteristics of the soil is not sufficient. Rossi et al. [19] found that the relationships between soil electrical resistivity and soil texture were linear while their effect on crop behaviour was strong but non- linear, therefore soil and crop data were both necessary for the correct identification of man- agement zones. A sophisticated “informed clustering” [23, 24] approach identifies management zones within a field based on a function fitted on crop response versus geophysical mapping; this way different zones correspond to a different type and extent of influence of soil properties on plant behaviour. Our simplified approach based on geophysical mapping has the drawback of not allowing such discrimination but it is fast and can be applied before vegetation data is available.

Based on our data, the rate of N should be corrected considering also the actual plants density or, more in general, on the basis of the actual status of the crop measured at the time of fertilization, by mean of indices of crop density/status such as NDVI, as already suggested by Benincasa et al. [33].

In our experiment zone 1 showed a significantly higher content of grain protein, yellow col- our, gluten, and N compared to both zones 2 and 3. As suggested by Diacono et al. [34], if this behaviour should be confirmed in subsequent years, the delineation of homogeneous areas taking quality into account could allow to segregate the harvested grain into different lots of semolina qualitative parameters. In all treatments, protein content was higher than 13.0%, therefore above the limit of 12.5% prescribed by the Italian law for a grain of good technological quality.

Regarding nitrogen uptake VRT showed high levels of N removal by the crop and a good protein content and other quality parameters in spite of lower N inputs, and this translated into a high nitrogen use efficiency. More specifically in VRT a large amount of the N given with the fertilizer was taken up by the crop, while in the case of UA 22% of the N applied was not, and therefore was left in the soil, and prone to leaching and pollution of deep soil/water. This has consequences on farm profitability but also on reducing environmental impact with respect to UA. Our results are in accordance with those of Diacono et al. [18], who found savings of 25% of the amount of fertilizer with variable rate fertilization without reducing yield or grain quality.

Table 4. *Qualitative traits and nitrogen use efficiency of durum wheat.*

Treatment	Grain Protein (%)	Grain Yellow Color	Grain Gluten (%)	Grain N (%)	Tot. N Uptake (kg ha^{-1})	NUE tot.
Zone 1	15. 7 a	14.9 a	11.7 a	2.7 a	112.0 a	0.82 b
Zone 2	13.3 b	14.5 b	10.2 b	2.3 b	63.6 b	0.6 b
Zone 3	13.9 b	14.5 b	9.7 b	2.4 b	114.9 a	1.3 a
Significance	**	**	**	**	***	**
UA	13.7 b	14.6	10.1 b	2.4	96.5	0.78 b
VRT	14.9 a	14.6	11.1 a	2.5	97.1	1.03 a
Significance	**	ns	**	ns	ns	**
Zone 1 x UA	15.0	14.9	11.1	2.6	110.2	0.92 b
Zone 1 x VRT	16.4	14.9	12.4	2.8	113.8	0.73 bc
Zone 2 x UA	12.9	14.5	9.4	2.22	60.1	0.5 c
Zone 2 x VRT	13.6	14.5	10.0	2.34	67.0	0.68 bc
Zone 3 x UA	13.3	14.5	9.7	2.28	119.3	0.92 b
Zone 3 x VRT	14.6	14.4	10.8	2.50	110.6	1.68 a
Significance	ns	ns	ns	ns	ns	***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' Significance at P<0.05; **, significance at P< 0.01; ns, no significant difference. Different letters indicate significant different.

Our data also suggest that where other limiting factors exist, applying high doses of N does not provide yield advantages and does not provide the best results in terms of efficiency. This does not agree with results of Guerrero et al. [17] who found that high N doses in low-yielding zones represent the best variable rate practice. In our case soil-based VRT was coherent with the principles of sustainability (less fertilizer, good qualitative-quantitative yield response and efficient use of the resources). The economic profitability of differential management has been questioned [35–37] with the argumenta that returns from PF technologies does not cover their costs or does not significantly change profitability [38], particularly when yield response to N does not vary strongly within the field [39]. However, in these analyses the positive effect of efficient resource use on environmental aspects and on down-side risk mitigation, are not taken into account [38]. Further research needs to consider such and other economic aspects: despite a general reduction of production costs and increase in gross margin, in accordance with Fabiani et al. [40] the high cost in machinery needed is a constraint to adopt VRT considering the generally small sizes of Italian farms. Also, the complexity of decisions from sensor data to agronomic management is one of the main challenges for the application of digitalization in agriculture. Simple approaches like the one presented in our study based on soil information versus more complex multi-data approaches may help simplify decisions and reduce costs.

Conclusions

In our experiment coupling geophysical mapping and traditional nitrogen balance was able to provide a quick basis for precision farming and VRT for N fertilization of wheat. Satisfactory production levels were reached by adapting the fertilization inputs to soil spatial variability. Yield and quality of UA was the same respect to VRT, but at the cost of more fertilizer, there- fore less efficient in resources use efficiency. Also, in VRT all the N given with the fertilizer was taken up by the crop, while in the case of UA 22% of the N applied was not, and was instead left in the soil and this implies a higher environmental risk of soil-water pollution.

Results from this research indicate that coupling geophysical mapping and traditional nitrogen balance may provide a quick basis for precision farming and VRT for N fertilization of wheat.

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Chapter 2. Validation of Rapid and Low-Cost Approach for the Delineation of Zone Management Based on Machine Learning Algorithms

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Abstract

Proximal soil sensors are receiving strong attention from several disciplinary fields, and this has led to a rise in their availability in the market in the last two decades. The aim of this work was to validate agronomically a zone management delineation procedure from electromagnetic induction (EMI) maps applied to two different rainfed durum wheat fields. The k-means algorithm was applied based on the gap statistic index for the identification of the optimal number of management zones and their positions. Traditional statistical analysis was performed to detect significant differences in soil characteristics and crop response of each management zones. The procedure showed the presence of two management zones at both two sites under analysis, and it was agronomically validated by the significant difference in soil texture (+24.17%), bulk density (+6.46%), organic matter (+39.29%), organic carbon (+39.4%), total carbonates (+25.34%), total nitrogen (+30.14%), protein (+1.50%) and yield data (+1.07 t ha^{-1}). Moreover, six unmanned aerial vehicle (UAV) flight missions were performed to investigate the relationship between five vegetation indexes and the EMI maps. The results suggest performing the multispectral images acquisition during the flowering phenological stages to attribute the crop spatial variability to different soil proprieties.

Keywords: machine learning; K-means; precision agriculture; zone management; validation; low- cost approach

Introduction

The current social context requires an increase in food production, improvement of its quality characteristics and greater environmental sustainability in the management of agricultural systems. Technological innovation plays a great role in making agriculture more efficient and sustainable.

On the 1 June 2018, the European Commission set goals for the new Common Agri- cultural Policy (CAP) for beyond 2020, focusing on the contribution of innovation and sustainability of crop production in Italy (through Regional Agricultural Policies), as for the rest of Europe (EIP-AGRI partnership). One of the key points reported is the necessity of effective nutrient management, more specifically, avoiding environmental losses and preserving yields [1].

Uniform management of fields does not consider spatial variability, and it is not the most effective management strategy. Precision agriculture is considered the most viable approach for achieving sustainable agriculture [2]. Soil is the temporal result of several factors such as the atmosphere, biosphere, lithosphere and hydrosphere [3]. Such variability may act over different spatial and temporal scales and affects crop yield both quantitatively and qualitatively [4].

The use of precision farming techniques (PA) is proposed as a solution, which would combine proximal and remote sensors [5] to follow and measure the spatial-temporal variability of the soil and crop during all growing seasons. Therefore, the soil plays a crucial role in the identification of zones within the field [6].

Among the different geophysical properties to better understand spatial variability of the soil, apparent electrical conductivity of the soil (ECa) is widely used by scientists [2,7,8] and is generally measured by electromagnetic induction (EMI) sensors. EMI has the advantages over traditional methods to collect soil information quickly, easily, at a relatively low cost and with a large volume of data collected [9].

The correct definition of management zones constitutes an important task to manage spatial variability within the field properly [10]. There are different techniques to delineate management zones taking into account soil or vegetation properties separately [11–13] or in combination, through classification techniques [10,13–16] or informed clustering based on functional relations [17,18], to account for response space-time dependence with spatially dense data, data misalignment in both space and time and repeated covariate measurements [18].

However, cluster analysis algorithms [19,20] are the basis of a direct approach to dividing a field using different layers of information stored in a geographical information system (GIS). Taking into account that data used to define management zones are usually related [15], it is possible to summarize the information by means of principal component analysis. Finally, the values of the main principal components can be interpolated and mapped, and these surfaces can be used to generate management zones by cluster analysis [11,12].

Irrespective of the approach used, defining an algorithm that will effectively partition a field in homogeneous zones remains one of the main challenges for precision agriculture [21]. Creating an algorithm requires the discretization and clustering of one or more continuous mapped variables that may influence yield in various, possibly non-linear ways. Several approaches were proposed in the literature, such as k-clustering, multivariate geostatistical methods [22,23], and GIS layering [24]. These approaches are powerful in their capacity to cluster high-dimensional datasets (i.e., including multiple variables), but they may not be easy to use because they do not offer a direct association of the classes to productivity or variability.

The cost-effectiveness of precision agriculture depends upon the cost of defining zones within fields, the temporal stability of these zones and the differences in responsiveness (yield and quality) of the zones submitted to differential treatment.

Delineation of management zones can be based on spatial variation in either crop yield or factors affecting the yield locally [23,25]. PA requires high-resolution spatial and temporal information, but traditional soil sampling and laboratory analyses are expensive, labor-intensive and require many samples [5]. By means of continuous soil and crop monitoring activity, the site-specific-nitrogen management (SSNM) can be applied [23]. The SSNM is based on the delineation of homogeneous zones within the field, between which different doses of fertilizer should be applied [9].

Particularly, SSNM is a form of precision agriculture whereby decisions on resource application and agronomic practices are improved to match soil and crop requirements better. The SSNM allows the division of a field into areas that have internally the same characteristics but differ from each other [19]. In order to produce the homogeneous zone map, we need to monitor the field over time by using several sensors. Depending on the type of sensor used and analysis performed, several authors provided different approaches to define the homogeneous zones. The authors of [26] proposed a multi-source geostatistical approach, [27] evaluated 20 different unsupervised machine learning algorithms, while [28] used the Self-Organizing Maps. The aim of our contribution is to validate the k-means algorithm to delineate homogeneous management zones. The k-means algorithm uses low-cost resistivity maps created by an electromagnetic induction method as a source of data. The proposed approach could be used to easily reconduct the spatial variability of the soil in homogeneous management zones statistically different from each other for high-quality prescriptions maps for the precision farming application.

Materials and Methods

Experimental Sites Description

The method was tested on two experimental sites (Figure 1). In both sites, three different homogeneous zones (ZH) were identified by resistivity maps created by an electromagnetic induction (EMI), which were subsequently identified with the letters a, b, c. In these three areas, two different fertilization applications were tested: variable rate (VRT) and uniform (UA).

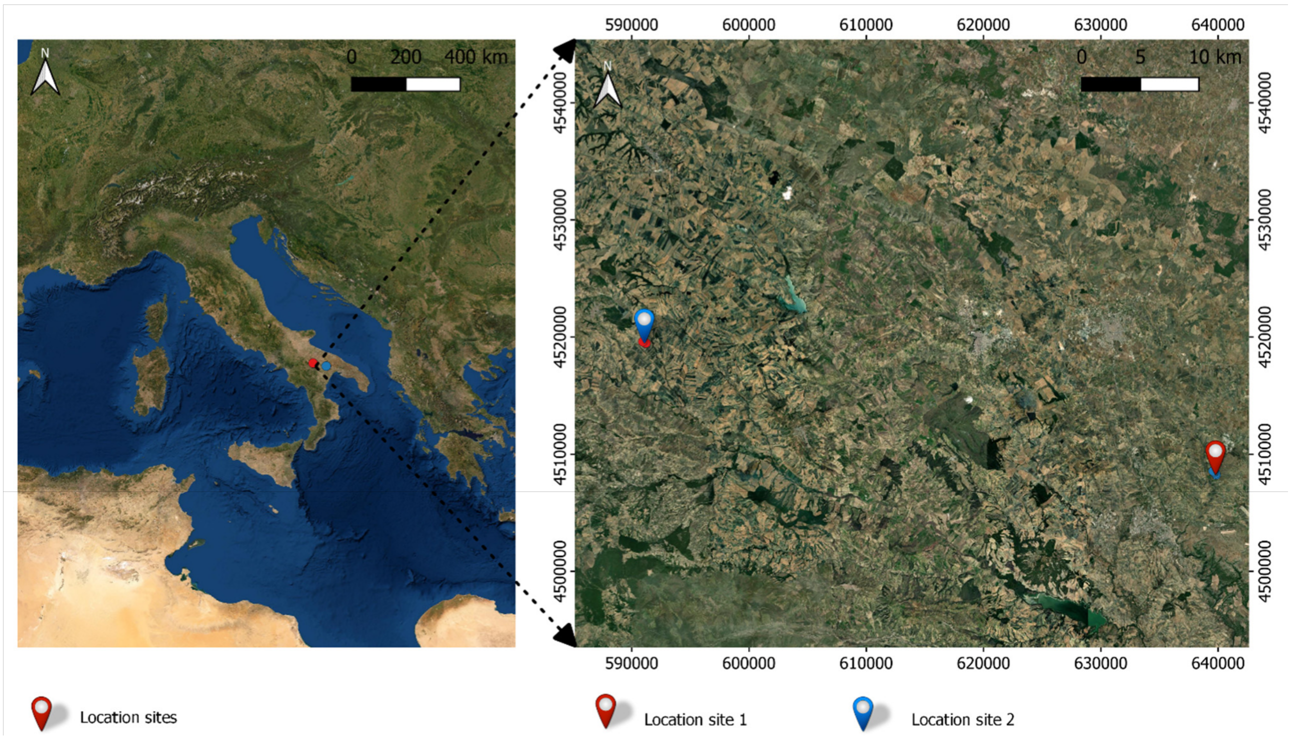

Figure 1. Location of experimental sites.

In 2019–2020 at site 1 Az. Agricola F.lli Lillo (Matera) latitude: 40.712640° longitude 16.656343° (Figure 2) on a study area of 6.65 ha, the experiment was conducted with durum wheat (*Triticum durum* L., var PR22D89) with sod seeding (7 January 2020).

In 2018–2019 at site 2 Genzano di Lucania (PZ) latitude: 40.82° N, longitude: 16.08° N (Figure 2), the study area (4.93 ha) was located on the clayey hills of the Bradanica grave and the basin of Sant'Arcangelo. The experiment was conducted with durum wheat (*Triticum durum* L., var Tirex). The inter-row spacing of 0.13 m and 250 kg ha^{-1} of seeds was used. Soil tillage consisted of a 40 cm deep plowing (28 August 2018) and two harrowing (11 November 2018 and 5 December 2018) with seeding (December 18 2018) (Figure 2).

The crop potential N uptake was estimated by the nitrogen content in the yield in each homogeneous area and was corrected considering the nitrogen provided by mineralization of the organic matter by using the agri-environmental measures adopted within the Rural Development Plans at a local scale (https://www.regione.marche.it/Regione-Utile/Agricoltura-Sviluppo-Rurale-e-Pesca/Produzione Integrata#Tecniche-Agronomiche, 15 December 2021). N mineralization was calculated considering the content of organic matter in the soil profile explored by the roots, its content in organic N and by the mineralization efficiency which in turn depends on the carbon/nitrogen ratio of the soil (1 for C/N < 9; 0.5 for C/N > 9, 0 for C/N < 12) (https://www.regione.marche.it/Regione-Utile/Agricoltura-Sviluppo-Rurale-e-Pesca/Produzione-Integrata#Tecniche-Agronomiche, 15 December 2021).

For the VRT treatment, the N doses applied in each area through a variable rate spreader are reported in Table 1 for site 1 and Table 2 for site 2. For each treatment, plots of 2 m × 2 m replicated three times inside each of the homogeneous areas identified in the field were established. In all such plots, a dose of N uniform was applied, which corresponds to the amount generally applied by the farmer and slightly over the average of the dose of N applied in the three zones. The fertilizer was manually spread in UA.

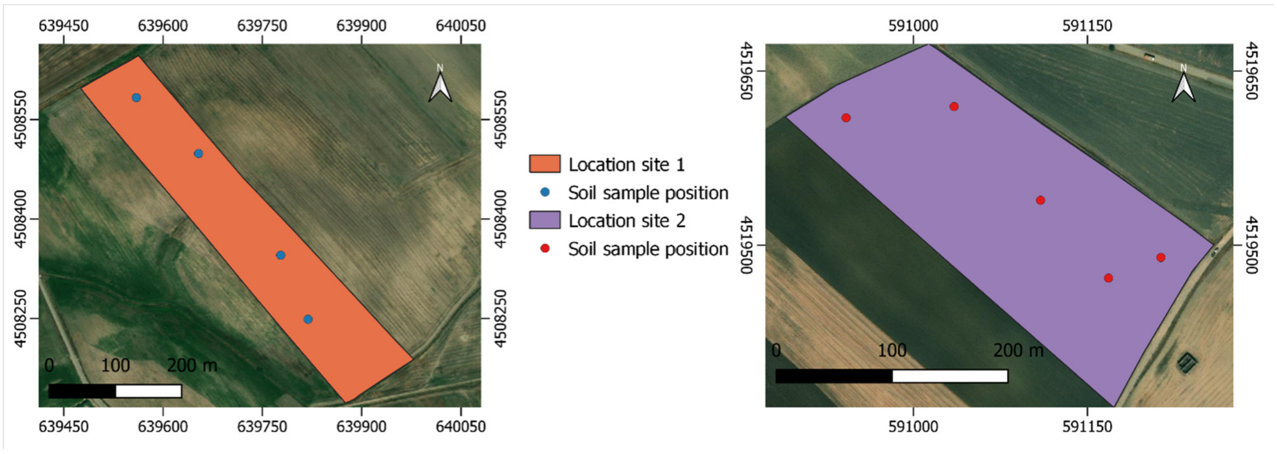

Figure 2. *Experimental site area visualization and relative soil sample position.*

Table 1. *Nitrogen management of site 1.*

Distribution Mode	Dose of Nitrogen (kg ha^{-1} N)
Uniform rate of application (UA) area a, b, c	150 kg ha^{-1} of N
Variable Rate (VRT)	Zone a: 78 kg ha^{-1} N + 40 kg ha^{-1} N (pre-sowing) = 118 kg ha^{-1} N tot. Zone b: 93 kg ha^{-1} N + 40 kg ha^{-1} N (pre-sowing) = 133 kg ha^{-1} N tot. Zone c: 99 kg ha^{-1} N + 40 kg ha^{-1} N (pre-sowing) = 139 kg ha^{-1} N tot.

Table 2. *Nitrogen management of site 2.*

Distribution Mode	Dose of N (kg ha^{-1} N)
Uniform rate of application (UA) area a, b, c	120 kg ha^{-1} of N
Variable Rate (VRT)	Zone a: 121.44 kg ha^{-1} N + 35 kg ha^{-1} N (pre-sowing) = 156.4 kg ha^{-1} N tot. Zone b: 63.44 kg ha^{-1} N + 35 kg ha^{-1} N (pre-sowing) = 98.3 kg ha kg ha^{-1} N tot. Zone c: 35.9 kg ha^{-1} N + 35 kg ha^{-1} N (pre-sowing) = 70.9 kg ha^{-1} N tot.

Soil and Crop Samples Position

The soil spatial variability was detected by means of low induction electromagnetic technique of CMD miniexplorer (GF Instruments, s.r.o., Brno, Czech Republic) with 6 m between transects and an average measurement distance of 0.8 m along transects.

The CMD miniexplorer returns data must be interpolated; in this case, the inverse distance squared method was performed by using Qgis [29–31].

After obtaining the electrical resistivity map, the cluster analysis was performed to identify the zones, and then for each zone, soil samples at the depths of 0–40 cm were collected and characterized by conventional analytical methods according to [32].

All samples were air-dried, and 2-mm sieved before laboratory analyses.

The organic carbon (OC) content was measured by the Walkley–Black method, and the total Kjeldahl nitrogen was determined by the Kjeldahl method. The available phosphorus (Pava) was determined by ultraviolet and visible (UV–vis) spectrophotometry according to the Olsen method. The total content of $CaCO_3$ was determined by the gas-volumetric methods (Freuling calcimeter method), whereas the active lime was extracted with 0.1 M ammonium oxalate and determined by titration with 0.1 M $KMnO_4$.

At crop maturity of durum wheat, the grain yield (t/ha) and protein content (%) were measured and then scaled to per hectare based on a sample area of 4 m², replicated three times for each homogeneous area. The protein content (%) of the grain was measured using the FOSS Infratec 1241.

Management Zone Delineation Approach

The management zones map creation workflow was entirely performed with R statistical software [33]. The workflow to generate the management zone map is composed of several steps, which could be summarized as (1) import resistivity map, (2) raster to dataframe conversion, (3) cluster analysis, (4) management zone map creation and (5) export. The resistivity maps were imported to R by using the “raster” function of the raster R package [34]. After checking the geographical reference system and the spatial resolution, the resistivity maps were converted to “dataframe” R object by using the “as.data.frame” function of the raster R package. The cluster analysis was performed by using the “kmeans” function of the stats R package [33]. The “kmeans” function requires the number of “centers” as a mandatory parameter, which defines the number of clusters that the algorithm must perform.

The optimal number of “centers” was defined by performing the gap statistic index, which calculates the goodness of clustering by comparing the total intra-cluster variation for different values of k with their expected values under the null reference distribution of the data. The gap statistic index was performed by using the “clusGap” function of the cluster R package [35].

Based on the gap statistic index, the k-means cluster analysis was performed, and the zone management map was created and converted to the spatial polygons data frame R object by using the “df_to_SpatialPolygons” function of the FRK package [36]. The spatial polygons data frame was exported by using the “writeOGR” function of the rgdal R package [37] in an ESRI Shapefile file format.

UAV Images Acquisition

The UAV images acquisition was conducted in 2019–2020 at site 1. The images were acquired using a Parrot Bluegrass drone with a Parrot Sequoia multispectral sensor, and the flight plan was set using Pix4Dcapute. Six flight missions were carried out throughout the durum wheat crop cycle (Table 3).

Table 3. *Flight missions date (dd mm yyyy) and relative phenological stages.*

Date	Phenological State
16 April 2020	Advanced tillering
5 May 2020	Beginning of stem elongation
12 May 2020	Advanced booting
10 June 2020	Inflorescence emergence
18 June 2020	Anthesis
10 July2020	Maturity

For the agriculture domain sector, each image acquired by UAV flight required an image processing workflow to compute the vegetation index (VI). The image processing is composed of three main steps: (1) orthomosaic reflectance map generation; (2) computation of VI maps; (3) data extraction.

Starting from the raw tiff files acquired by the UAV, the orthomosaic reflectance map was generated by using structure from motion (SfM) software [38], which in this case was PIX4D.In order to complete the second main step, the orthomosaic reflectance map was imported in R statistical software [33], and the VI shown in Table 4 was calculated [39].

Table 4. *Vegetation indexes formulas and references.*

Vegetation Index	Formula	References
MSAVI2	$MSAVI2 = \frac{2*NIR+1-\sqrt{(2*NIR+1)^2-8(NIR-Red)}}{2}$	[40]
NDRE	$NDRE = \frac{NIR-Red\ Edge}{NIR+Red\ Edge}$	[41]
NDVI	$NDVI = \frac{NIR-Red}{NIR+Red}$	[42]
EVI2	$EVI2 = 2.5 * \frac{NIR-Red}{NIR+(2.4*Red)+1}$	[43]
WV.VI	WV.VI = $NIR^2$2=+RedRed NIR	[44]

In order to define the relationship between the previous VI and the resistivity map, the coefficient of determination (R^2) was computed. (1) The VI maps were scaled at the same resolution as the resistivity map by using the "resample" function of the raster R Package [34]. (2) After obtaining raster files with the same resolution, they were converted to a data frame by using the "as.data.frame" function of the raster R Package [34]. (3) Then, a linear model was fitted by using the "lm" function of the stats R Package [33] in order to compute the R^2.

Statistical Analysis

All the statistical analyses were performed with R statistical software [33]. Before performing any analysis, a descriptive statistics analysis was performed on the resistivity maps; the range and the coefficient of variation (CoV) to describe the spatial variability of both sites were calculated.

In order to validate the zone management map creation workflow, the statistical analysis was performed on the soil samples, which were assigned an experimental factor in relation to the zone management area previously defined. In order to perform the statistical analysis, a one-factor linear model was built by using the "lm" function of the stats R package [33], on which the cluster was considered the main factor.

Before performing the Analysis of Variance (ANOVA), whether the model met the three assumptions of the ANOVA was verified [45]. The Normality distribution of the model residual was checked both graphically (QQ-plot) and by performing the Shapiro–Wilk normality test. Moreover, the homoscedasticity was checked using the Levene test. The last ANOVA assumption was satisfied by the experimental design and the random sampling. When all the three ANOVA assumptions were met, the ANOVA was applied to the model. Only when the ANOVA showed a significant difference (*p*-value < 0.05), the estimated marginal means post hoc analysis was performed by using the "emmeans" function with the Bonferroni adjustment of the emmeans R package [46]. For the yield dataset, the same procedure of the soil samples dataset was performed, except that the statistical analysis was performed on a full factorial model where the site and zone management were set as experimental factors.

Results

Resistivity Maps

The resistivity maps of both sites are shown in Figure 3. The values were scaled based on quartiles to show the in-field spatial variability better. Based on the previous scale classification, both sites showed high spatial variability. As evidence of the different spatial variability, both range and coefficient of variation (CoV) were calculated (Table 5). The first site obtained a higher value of +15.11 CoV and +18.56 of range than the second site. While considering the EC value, the first site obtained a higher value of +3.90 mS m^{-1} than the second site (Table 5).

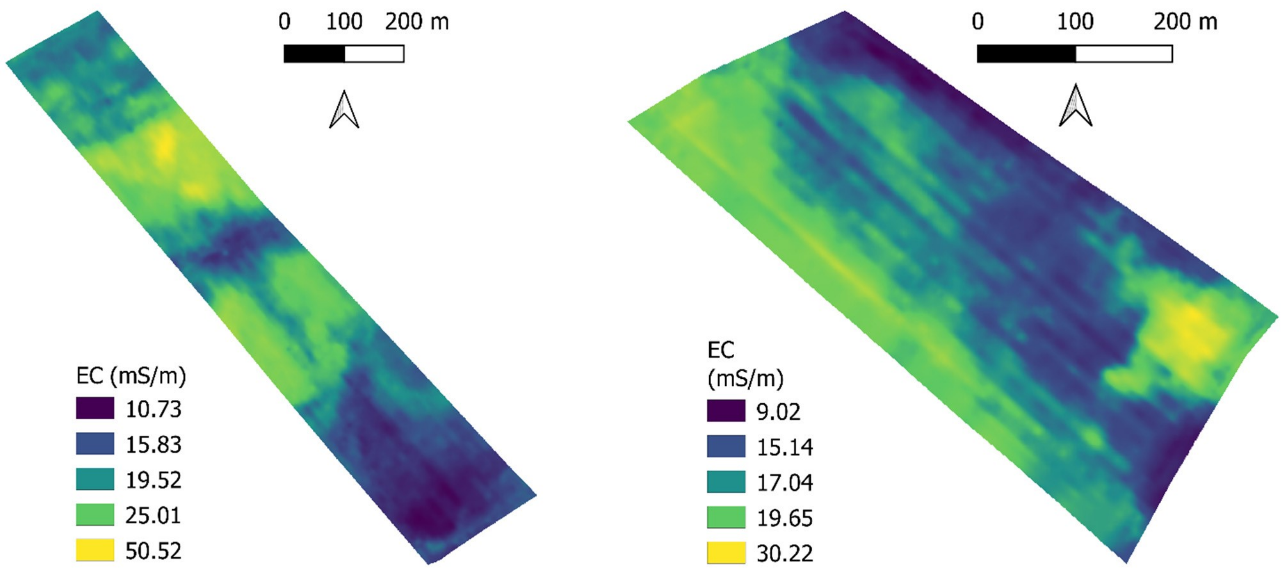

Figure 3. Resistivity map of the first site (Matera on the left) and of the second site (Genzano).

Table 5. Descriptive statistics of EC for both sites.

Site	EC					
	Mean	Dev Std	CoV [1]	Min	Max	Range
1	21.40	7.28	34.02	11.00	51.00	39.76
2	17.50	3.31	18.91	9.00	30.00	21.20

[1] CoV: Coefficient of variation.

Zone Management Delineation and Statistical Analysis Results

The number of the optimal "centers" to associate as a parameter for the k-means computation was defined based on the gap statistic index. For both sites, the gap statistic index defined that the optimal number of clusters was two. The zone management map visualization is reported in Figure 4. In order to agronomically validate the two zones identified by the k-means classification for both sites, we set an experimental factor of the soil samples based on the affiliation of zone management. Then the zone management experimental factor was analyzed by the ANOVA applied to the soil sample.

The ANOVA showed that the zone management defined by the k-means was statistically significant for clay, silt, bulk density, EC, organic matter, organic carbon, total carbonate, nitrogen and ratio C/N for both sites (Tables 6–8).

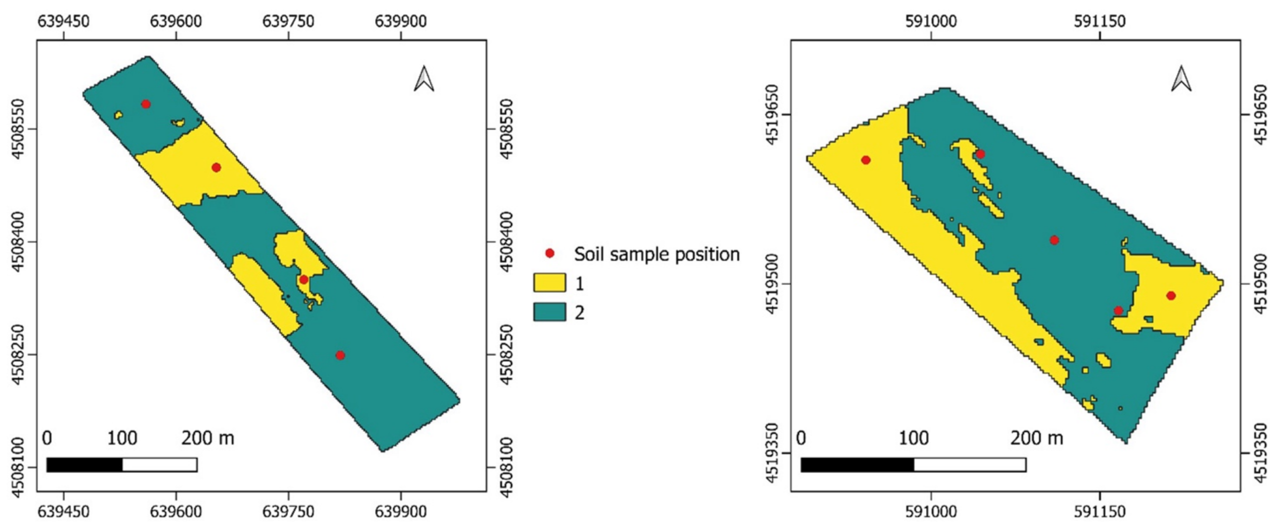

Figure 4. *Zone management maps for both sites and relative soil samples position.*

Table 6. *Results of the ANOVA applied to the soil samples based on the zone management experimental factor for both sites.*

Site	Factor	Df [1]	Clay	Silt	Sand	Bulk Density
1	ZM [2]	1	*	*	0.98	*
2	ZM	1	*	*	*	*

[1] df: Degree of freedom; [2] ZM: Zone management; *: Significant at $p < 0.05\%$.

Table 7. *Results of the ANOVA applied to the soil samples based on the zone management experimental factor for both sites.*

Site	Factor	Df [1]	EC [2]	Organic Matter	Organic Carbon	Totale Carbonetes	Nitrogen	C/N [3]
1	ZM [4]	1	*	*	*	*	*	*
2	ZM	1	*	*	*	*	*	*

[1] df: Degree of freedom; [2] EC: Electrical conductivity; [3] C/N: Ratio carbon–nitrogen; [4] ZM: Zone management; *: Significant at $p < 0.05\%$.

Table 8. *Results of the ANOVA applied to the soil samples based on the zone management experi- mental factor for both sites.*

Site	Factor	Df [1]	Mg/K [2]	Na	Mg	P	AWC [3]	pH
1	ZM [4]	1	0.27	0.4	0.27	0.52	0.96	0.97
2	ZM	1	0.9	0.11	*	0.14	0.34	0.72

[1] df: Degree of freedom; [2] Mg/K: Ratio Magnesium potassium; [3]AWC: Available water content; [4] ZM: Zone management; *: Significant at $p < 0.05\%$.

In addition to the variables previously cited, for the second site, the ANOVA showed a statistical impact of zone management for sand and magnesium (Tables 6–8). However, the ANOVA did not show a statistical impact of the zone management for the ratio Mg/K, sodium, phosphorus, AWC and pH. The emmeans with the Bonferroni adjustment analysis showed that, for both sites, zone number 2 obtained a statistically higher value than zone number 1 for clay, EC, organic matter, organic carbon, nitrogen and ratio C/N. However, no statistical superiority was highlighted between the two zones of both sites for Mg/K, phosphorus, AWC and pH (Tables 9 and 10).

Table 9. *Results of the emmeans function applied to the soil samples based on the zone management experimental factor for both sites.*

Site	ZM [1]	Clay		Silt		Sand		Bulk Density		EC [2]		Organic Matter		Organic Carbon		Total Carbonates	
		Mean	Dev Std	Mean	Dev Std	Mean	Dev Std	Mean	Dev Std	Mean	Dev Std	Mean	Dev Std	Mean	Dev Std	Mean	Dev Std
1	1	33.80 b	3.11	43.05 a	8.56	23.15 a	11.67	1.36 a	0.01	0.17 b	0.04	1.62 b	0.06	0.94 b	0.04	35.62 a	2.24
	2	41.70 a	2.55	35.45 b	0.64	22.85 a	1.91	1.28 b	0.02	0.11 a	0.06	2.39 a	0.25	1.39 a	0.15	26.97 b	2.23
2	1	27.00 b	11.31	27.00 b	2.83 33.33 a	46.00 a	14.14	1.42 a	0.09	0.19 b	0.04	1.03 b	0.71	0.60 b	0.41	20.65 a	12.52
	2	37.67 a	3.06	3.21		29.00 b	2.65	1.32 b	0.02	0.23 a	0.01	1.92 a	0.24	1.12 a	0.14	15.20 b	9.61

[1] ZM: Zone management; [2] EC: Electrical conductivity. Means within column that are followed by the same letter are not significantly different at $p < 0.05\%$.

Table 10. *Results of the emmeans function applied to the soil samples based on the zone management experimental factor for both sites.*

Site	ZM [1]	Nitrogen		C/N [2]		Mg/K [3]		Na		Mg		P		AWC [4]		pH	
		Mean	DEV Std	Mean	Dev Std	Mean	Dev Std	Mean	Dev Std	Mean	Dev Std	Mean	Dev Std	Mean	DEV Std	Mean	Dev Std
1	1	1.50 b	0.04	6.25 b	0.35	1.26 a	0.06	0.06 a	0.01	0.83 a	0.02	10.00 a	2.83	147.5 a	12.02	8.35 a	0.07
	2	1.79 a	0.05	7.75 a	0.64	3.46 a	1.57	0.14 a	0.11	2.57 a	1.61	12.50 a	3.54	148.00 a	5.07	8.35 a	0.07
2	1	0.66 b	0.37	8.76 b	1.25	4.13 a	1.56	0.20 b	0.04	2.08 b	0.35	6.50 a	0.71	85.50 a	7.78	8.20 a	0.14
	2	1.18 a	0.06	9.41 a	0.74	3.96 a	1.07	0.60 a	0.23	3.67 a	0.34	9.00 a	1.73	94.33 a	9.02	8.17 a	0.06

[1]ZM: Zone management; [2] C/N: Ratio carbon–nitrogen; [3] Mg/K: Ratio Magnesium potassium; [4] AWC: Available water content. Means within column that are followed by the same letter are not significantly different at $p < 0.05\%$.

Furthermore, for site 1, zone 2 obtained a higher percentage value of +18.95% of clay, +35.29 % of EC, +32.22% of organic matter, +32.37% of organic carbon, +16.20% of nitrogen and +19.35% ratio C/N than the zone 1. While zone 1 obtained a higher percentage value of +17.65 of silt, +5.88 % bulk density and +24.28% of total carbonates than zone 2 (Tables 9 and 10).

For site 2, zone 2 resulted statistically superior for +28.32% of clay, +18.99% of silt, +17.39% of EC, +46.35% of organic matter, +46.43% of organic carbon, +44.07% of nitrogen,

+6.91% of ration C/N and +66.67% of sodium than zone 1 (Tables 7 and 8). However, zone 1 showed a statistically higher for +36.96% of sand, +7.04% of bulk density and +26.39% of total carbonates than zone 2.

Based on the results obtained above, it can be stated that zone 2 generated by the cluster analysis for both sites has soil physical and chemical characteristics superior to zone 1 for durum wheat cultivation, such as higher clay, silt, EC, organic matter, organic carbon, nitrogen and the ratio of carbon and nitrogen.

Grain Yield and Statistical Analysis

The ANOVA applied to the full factorial model showed that the single effect of site and zone management statistically impacts the grain yield (t/ha) and grain protein content (%). Moreover, the combined effect of the interaction between site and zone management statistically impacted the grain yield (t/ha), while for the protein content, no statistical impact was raised (Table 11). Since we observed a significant difference in the combined effect, we applied the post hoc analysis on the site and zone management interaction.

Table 11. *Results of the ANOVA applied to the grain yield and protein content on the zone management experimental factor for both sites.*

Experimental Factor	Df [1]	Grain Yield (t/ha)	Protein (%)
		***p* Value**	***p* Value**
Site	1	***	***
ZM [2]	1	*	***
Site × Zone	1	***	0.11

[1] df: Degree of freedom; ZM: Zone management; *: Significant at $p < 0.05\%$; ***: Significant at $p < 0.001\%$.

With reference to the production (grain yield t/ha), the ML approach shows for both sites 1 and 2, and for both fertilization application N (UA) and N (VRT) a difference between management zones 1 and 2 (Table 12). Specifically, in site 1 in N (UA), zone 2 shows the production of +0.95 t/ha with respect to zone 1; in zone 2 in N (VRT), it produced +0.7 t/ha with respect to zone 1.

Furthermore, in site 2 in N (UA), zone 2 produced + 1.4 t/ha with respect to zone 1; in N (VRT), zone 2 produced + 1.25 t/ha with respect to zone 1 (Table 12). The same is true for the % of grain proteins content where the difference is relevant for both site 1 and site 2 between management zones 1 and 2 defined with ML. In line with the results described, it is possible to underline that in the ZH approach for both sites with reference to production (grain yield t/ha), even considering the N (UA) and N (VRT) treatments, a significant difference is highlighted between zone c with respect to zones a b. This reinforces the results obtained from the test of the approach (ML) as zones a b flow into zone 2, and zone c flows into zone 1 (Table 12).

Table 12. *Results of the emmeans function applied to the grain yield and protein content based on the zone management experimental factor for both sites.*

N	Approach	Zones	Site 1		Site 2	
			Grain Yield t ha^{-1}	Protein %	Grain Yield t ha^{-1}	Protein %
			Mean	Mean	Mean	Mean
UA	ZH	c	5.2 b	14.1 a	1.7 b	12.9 b
		b	6.0 a	12.2 b	3.1 a	15 a
		a	6.3 a	12.4 b	3.2 a	13.3 b
	ML	1	5.2 b	14.1 a	1.7 b	12.9 b
		2	6.15 a	12.3 b	3.1 a	14.2 a
VRT	ZH	c	4.8 b	13.7 a	1.8 b	13.6 b
		b	5.6 a	12 b	2.9 a	16.4 a
		a	5.5 a	13. 2 a	3.2 a	14.6 b
	ML	1	4.8 b	13.7 a	1.8 b	13.6 b
		2	5.5 a	12.6 b	3.05 a	15.5 a

Means within column that are followed by the same letter are not significantly different at $p < 0.05\%$.

Relationship between Vegetation Index and Resistivy Map

Six UAV flight missions were performed during all growing seasons in site 1 to obtain multispectral images to compute five vegetation indexes and evaluate the relationship with the resistivity map. As reported in Table 13, the coefficient of determination of the relationship between the vegetation indexes and the resistivity map is not significant until flowering.

Table 13. *Coefficient of determination (R^2) of the relationship between the vegetation indexes and the resistivity map during all growing seasons*.

Vegetation Index	Date					
	16 April 2020	5 May 2020	12 May 2020	10 June 2020	18 June 2020	10 July 2020
NDRE	0.05	0.01	0.04	0.52	0.28	0.03
NDVI	0.02	0.01	0.08	0.56	0.35	0.02
MSAVI2	0.02	0.01	0.07	0.55	0.30	0.01
EVI2	0.02	0.01	0.06	0.55	0.31	0.01
WV.VI	0.03	0.02	0.11	0.45	0.23	0.01

During flowering, the maximum value of correlation is reached with an average coefficient of determination of 0.53. After flowering, the correlation value decreases for each vegetation indexes until the maturity of the durum wheat, where a non-significant correlation is shown (Table 13). The vegetation index that showed a higher relationship with the resistivity map is the NDVI [40], which reached an R^2 of 0.56 during flowering, while the vegetation index that reported the lowest R^2 was the WV.VI.

The NDVI maps are reported in Figure 5, which were scaled by using the quartile and where it is possible to appreciate the evolution of the NDVI throughout the year. All the NDVI maps were scaled by using the quartile. While in Figure 6, it is possible to appreciate the overlapping of the resistivity map, NDVI and the zone management defined by the cluster analysis.

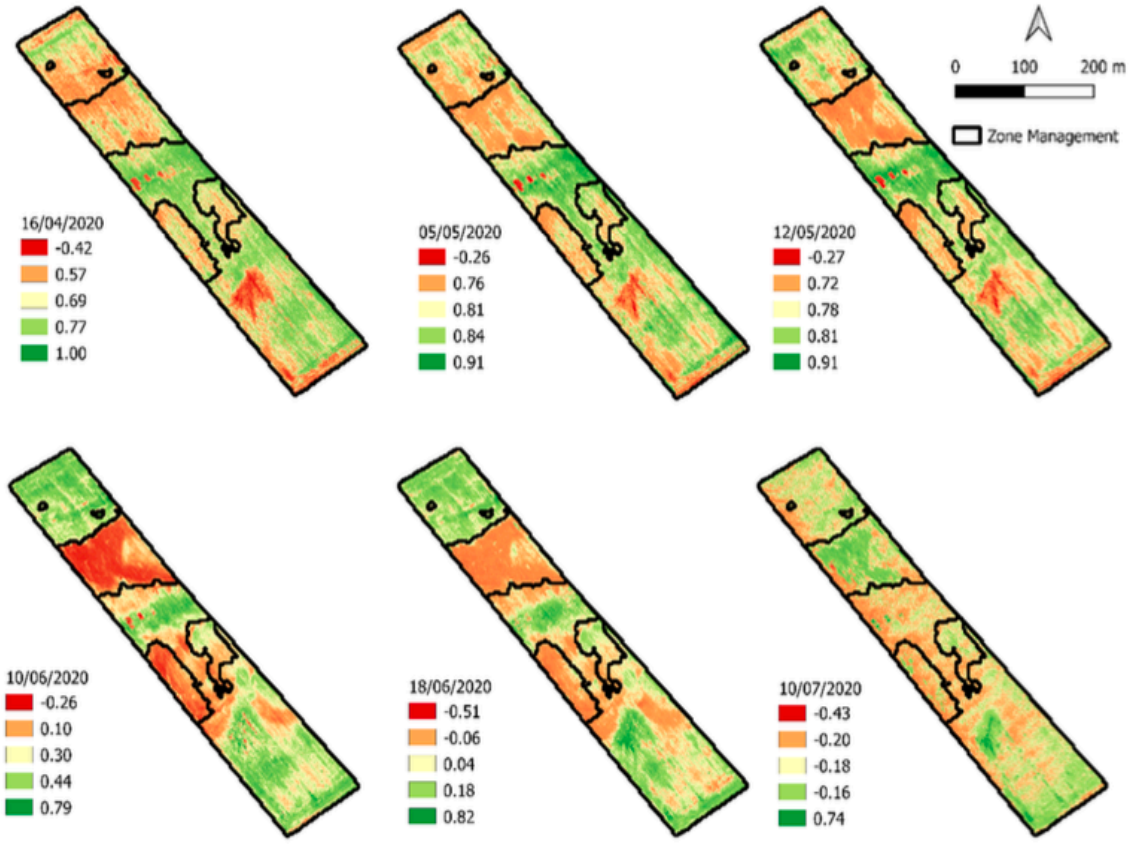

Figure 5. The NDVI maps reported for all growing seasons at site 1.

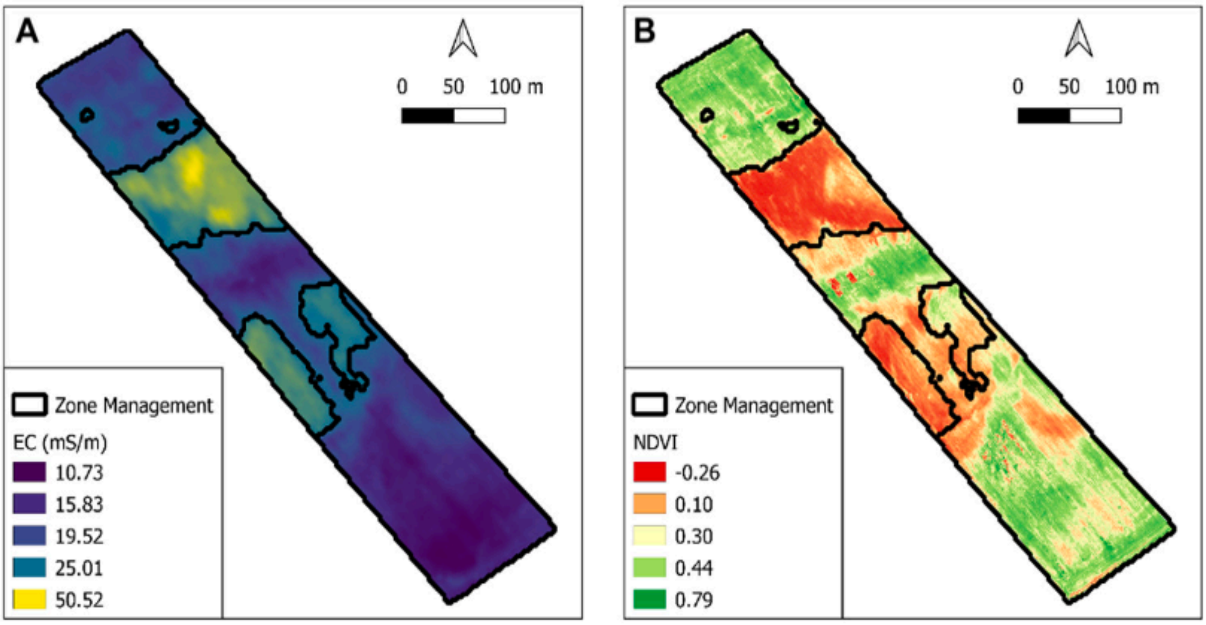

Figure 6. Overlapping of the resistivity map (**A**) and NDVI during flowering (**B**) and the zone management defined by the cluster analysis.

Discussion

Soil Sensor and Management Zone Creation

Proximal soil sensors are receiving strong attention from several disciplinary fields, and this has led to a rise in the number of proximal soil sensors available in the market in the last two decades [47]. These sensors contribute to measuring the spatial-temporal variability of soil proprieties, such as moisture content and soil texture [48].

These sensors could be used to measure the soil organic matter, nitrogen availability and the ratio of carbon–nitrogen indirectly, which are soil variables that are mostly considered to calculate the nitrogen balance in several integrated production standards [49]. Moreover, after careful evaluation and calibration, these sensors can avoid time-consuming and expensive soil sampling and analysis, which cannot be scaled at the farm level [50]. Based on previous assumptions, it is essential to use the proximal soil sensor in order to characterize the soil proprieties and to perform the SSNM (Site-Specific Nitrogen Management) [19]. By using the EMI sensor, we could generate the resistivity map, which can be used as the information layer to define the zone management. Different approaches such as the multivariate geostatistical approach [51] or the machine learning approach were found in the literature, which deal well with non-linear patterns [27,52].

Our contribution is to validate agronomically the k-means algorithm to delineate zone management which uses the resistivity map by using a statistical approach. Both sites under study showed a different spatial variability which allowed us to validate the approach in two different field conditions. The unsupervised machine learning algorithm, which was the k-means [53] based on the gap statistic index [35], reported the existence of two zone managements at both sites.

At both sites, multiple soil and crop samples were performed in those different zones in order to perform a statistical analysis to agronomically validate the presence of the two zones [54]. At both sites, between the two zones, there was a significant difference in clay (%), silt (%), bulk density (g m^{-3}), EC (mS m^{-1}) organic matter (%), organic carbon (%), total carbonates (%), nitrogen (g kg^{-1}) and C/N. The second zone for both sites showed a higher value of organic matter, organic carbon, nitrogen and ratio of nitrogen and carbon, which led to higher grain yield (t ha^{-1}) than the first zone. This result is in accordance with [55], where a higher content of soil organic matter and nitrogen led to a higher value of several vegetation indexes and grain yield (t ha^{-1}). Moreover, it was observed that the differences in yield are significant between zones and not within zones. While for the grain protein content (%), the difference was found only in the two sites where the resistivity map obtained a higher spatial variability.

Relationship between Vegetation Indexes and Resistivity Map

Efficient and reliable methods for measuring spatial variability in soil properties are fundamental in precision agriculture [56]. It is by using these instruments precisely that spatial variability can be estimated without soil sampling, which is time–money consuming [50]. Beyond the use of proximal soil sensors, several authors tried to use remote sensing data, such as Sentinel-2 multispectral images, in order to predict the spatial soil proprieties, such as organic carbon [57] and electrical conductivity [58]. Other authors tried the Pedotransfer Functions [59] or neural networks [60] in order to improve the accuracy of the models. We showed that the correlation between the VI and the resistivity map depends strongly on the phenological and developmental stage of the durum wheat. During the whole development of the crop, there is no significant correlation, except during flowering when the linear correlation reaches 0.53 of the R^2. This is because flowering is the most important and susceptible phase of crop phenological development. During flowering, the crop reaches its maximum development, generating maximum leaf development.It is at that point that differences in nitrogen uptake due to soil differences are shown in the crop [5]. Moreover, NDVI was the best vegetation index to be related to the resistivity map, while the worst VI was the WV.VI.

Conclusions

Two sites were mapped through an electromagnetic induction sensor to measure the electric conductivity map. An unsupervised machine learning approach was applied to the resistivity maps to detect the presence of different zones. Based on the results of the classification algorithm, multiple soil and crop samples were taken to validate the difference of the zones agronomically.

The algorithm used was able to detect the presence of the two zones for both sites. The soil samples acquired showed a significant difference between zones and not within zones for organic matter, nitrogen and the ratio of carbon–nitrogen. The differences reported on the soil proprieties led to a statistical difference in the grain yield obtained between the zones detected by the k-means algorithm.

This approach could be used to provide a high-quality prescription map to apply the precision agriculture applications. This approach could be scaled at the farm level; one resistivity survey and a few soil samples could generate a high-quality prescription map, containing costs and falling within the farm-year budget. Future work will focus on creating an automated nitrogen fertilization determination method starting from the acquired soil data.

Moreover, the correlation between the VI and resistivity map depends strongly on the phenological and developmental stage of the durum wheat. Therefore, we suggest performing the UAV multispectral images acquisition during the flowering phenological stages to attribute the crop spatial variability to different soil conditions.

Author Contributions*:* Conceptualization, M.D., M.F. and M.P.; methodology, M.D. and M.F.; validation, M.P., L.L., P.A.D., R.O. and S.Z.; formal analysis, M.D. and M.F.; resources, M.P.; data curation, M.D.; writing—original draft preparation, M.D. and M.F.; writing—review and editing, M.D., M.F., M.P.; supervision, M.P.; project administration, M.P.; funding acquisition, M.P. All authors have read and agreed to the published version of the manuscript.

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Chapter 3. Precision nitrogen management in rainfed durum wheat cultivation: exploring synergies and trade-offs via energy analysis, life cycle assessment, and monetization.

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Abstract

Fertilization with variable rate technology (VRT) is a pivotal technique of precision agriculture proposed for eco-friendly farming practices. Yet the magnitude of environmental benefits is often not well known or is highly variable. This study used a multi-indicator model and life cycle-based indicators to compare the performance of rain-fed durum wheat production using uniform (UA) and variable N fertilization (VRT). Two functional units were used: 1 ha of cultivated wheat and 1 ton of wheat produced. The energy analysis indicated that VRT increases energy use efficiency and productivity by 13.3%, reduces specific energy and total energy input by 11.7%, and increases net energy gain by 15.3%. The life cycle assessment (LCA) analysis indicated that for some environmental impacts, VRT had minor negative effects due to the comparable yield performance with UA. Yet, the VRT had a noteworthy positive impact on global warming, fine particulate matter formation, stratospheric ozone depletion, terrestrial acidification, and marine eutrophication, generating a final environmental benefit of 12.2% for 1 ton of product and 13.3% for 1 ha of land. Economic valuation or monetization of LCA results using monetization weighting factors indicated indirect economic benefits of VRT can be up to 6.6% for 1 ton of product and 7.7% for 1 ha of land. Our findings support the use of nitrogen fertilization with VRT for sustainable extensification and improved eco-efficiency of wheat production in a Mediterranean context. As a result of our research, we conclude that future case studies on annual crops with moderate land requirements should employ multiple metrics and functional units, as well as the concepts of monetization and life cycle assessment, to investigate trade-offs between yield, economic, and environmental benefits and to aid decision-making about the true sustainability of proposed farming technologies.

Keywords Life cycle assessment (LCA) · Precision agriculture · Site-specific input management · Nitrogen variable rate application · External cost

Introduction

Agriculture and food systems are confronted with daunting and complex challenges, not the least of which is the ongoing effort to increase food production by 25–70% above cur- rent levels while maintaining and enhancing ecosystem resilience (Hunter et al., 2017). Traditional farming practices, on the other hand, are still used to manage an agricultural field uniformly, ignoring the inherent variability in topography, soil, crop growth conditions, and other agronomic factors (Neupane & Guo, 2019). As a result, the excessive and inappropriate use of agrochemicals, fossil fuels, natural resources, and machinery is jeopardizing the ecological integrity of agroecosystems (Singh & Singh, 2017). The prevailing discourse on the future of agriculture calls for food production to increase while becoming more environmentally sustainable (Hunter et al., 2017). Sustainable intensification is emerging as the most frequently referenced new paradigm to produce more from the same area of land by increasing efficiency, reducing waste, conserving resources, reducing negative impacts on the environment, and enhancing the provision of ecosystem ser- vices (Wezel et al., 2015). Sustainable intensification is achieved through increased inputs, improved agronomic practices, improved crop varieties, and other innovations (Tilman et al., 2011).

Precision agriculture (PA) is widely acknowledged as a contributor to farming efficiency and environmentally friendly farming practices, and it is essential to long-term intensification (Lindblom et al., 2017). It assists farmers in making precise and optimized use of crop-specific inputs, resulting in lower production costs and a lower environmental impact (Bacenetti et al., 2020; Canaj et al., 2021). Nitrogen (N) is an essential and often the most yield-limiting nutrient for winter wheat production. However, often N fertilization in wheat is commonly based on yield goals, derived by applying uniform rates without considering the spatial and temporal variability (Gobbo et al., 2022). As a result, the N supply and crop demand are misaligned, resulting in low time and space efficiency (Denora et al., 2022) and economic and environmental losses (Fiorentino et al., 2020; Gobbo et al., 2022). The precise management of N fertilizer application is essential for improving crop productivity, use efficiency and environmental sustainability. Variable-rate technology (VRT) is a piv- otal technology in PA, aiming to perform site-specific chemical, lime, gypsum, irrigation water, and other farm input management across a field (Vatsanidou et al., 2020). Because it tackles in-field heterogeneity in soil N availability and crop response, variable rate fertili- zation provides a technique for more effective site-specific management (Stamatiadis et al., 2018). The empirical findings suggest that variable-rate fertilizer application can have both environmental and economic benefits. Many studies, however, fail to investigate the links between the environment and production, as well as the environmental and economic implications of the product's life cycle. Precision agriculture frequently necessitates the use of advanced machinery and technological systems, the construction, maintenance, and use of which may reduce the potential environmental and economic benefits of its implementa- tion (Bacenetti et al., 2020).

The life cycle thinking has been considered one of the most fitting methodologies to deal with farming sustainability. Life cycle assessment (LCA) is widely regarded as the most effective method for assessing the impact of crop production-related emissions and resource consumption. It generates a better understanding of the energy, water, and mate- rial inputs and evaluates the output impacts of any production system from a life cycle per- spective. LCA has been carried out on various precision agriculture applications, including irrigation (Canaj et al., 2021; Fotia et al., 2021); fertilization (Bacenetti et al., 2020; Jovarauskas et al., 2021; Li et al., 2016; Meza-Palacios et al., 2020; Sanches et al., 2021; Vat- sanidou et al., 2020); mechanized field operations (Ashworth et al., 2022; Lagnelöv et al., 2021; Lovarelli & Bacenetti, 2017); and land leveling (Nguyen-Van-Hung et al., 2022). It is applied to olives in Greece (Fotia et al., 2021; van Evert et al., 2017), zucchini in Italy (Canaj et al., 2021), rice in Italy (Bacenetti et al., 2020) and Asia (Nguyen-Van-Hung et al., 2022), pear orchards in Greece (Vatsanidou et al., 2020), nectarines in Greece (Núñez- Cárdenas et al., 2022), corn in the USA (Li et al., 2016), vineyards in Greece (Balafoutis et al., 2017; Pradel et al., 2022), wheat in Lithuania (Jovarauskas et al., 2021) and sugar- cane in Brazil (Sanches et al., 2021) and South Africa (Van Der Laan et al., 2015). Previous LCA studies in wheat production (Fabiani et al., 2020; Jovarauskas et al., 2021; Kazlauskas et al., 2021; Medel-Jiménez et al., 2022; Scuola et al., 2017) found that variable fertiliza- tion rates may reduce overall energy consumption and greenhouse gas (GHG) emissions. However, other direct and indirect environmental benefits from the reduction of synthetic resources in crop production could be realized. Understanding how alternative agricultural input efficiency, such as variable rate fertilization, contributes to a variety of environmental effects is essential for reducing crop production’s environmental impact. This study applied life cycle energy analysis (LCEA) and a multi-indicator life cycle assessment (LCA) to evaluate the energy performance, environmental impact, and external environmental costs of durum wheat production in southern Italy by using different N fertilization strategies: variable rate technology (VRT) and uniform application (UA). The findings provide the first detailed assessment of the energy and environmental benefits that can be realized when precision farming technologies are used to support N fertilization in rainfed wheat production in a Southern Mediterranean context. Moreover, the study is the first of its kind to estimate the indirect economic benefits of variable rate fertilization in cereal crops by monetizing the LCA results.

Material and methods

Case study and system description

The data for this study were retrieved from field data collected in 2018–2019 at Genzano di Lucania (Potenza province, Basilicata region), latitude: 40.82° N, longitude: 16.08° N. The Basilicata region primarily produces cereals, accounting for 72% of arable land. The experimental field had a total area of 4.07 ha^{-1}. The area is located on the clayey hills of the Bradanica grave and the basin of Sant'Arcangelo (Fig. 1).

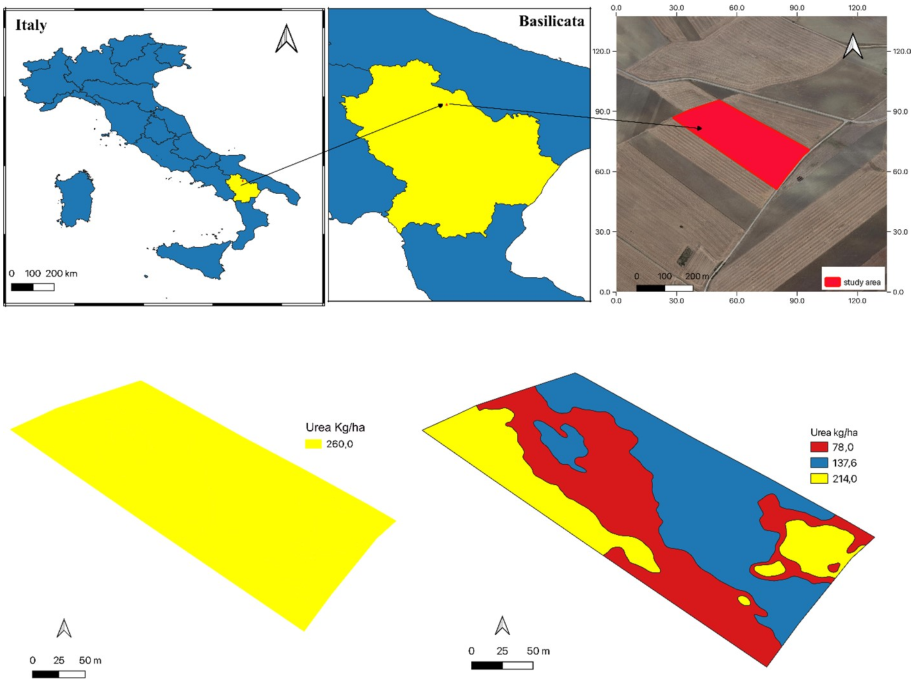


Fig. 1 *Location of the study site and delineated maps of N fertilization in uniform management and variable-rate application*

Across the whole field durum wheat (*Triticum durum L.*, var. Tirex) was sown with inter row spacing of 0,13 m and 250 kg ha^{-1} of seeds were used. Soil tillage consisted in a 40 cm deep plowing (August 28, 2018) and two harrowing (November 11 2018 and December 5 2018) with seeding (December 18 2018).

Pre-sowing fertilization was broadcast applied with 92 kg ha^{-1} of P_2O_5 and 36 kg ha^{-1} of N. A dose of 35 kg ha^{-1} of N (Urea 46%) was spread in pre-sowing over the entire field. In the uniform application (UA) plots, we applied a dose of N equal to 85 kg ha^{-1}, which corresponds to the amount generally applied by the farmer, and slightly over the average, the dose of N applied in the three zones. The amount of nitrogen fertilizer to be applied by VRT was calculated based on estimated crop nitrogen uptake and soil characteristics of the area determined by electrical resistivity (Denora et al., 2022).

Crop potential N uptake was estimated using the previous year's crop yield in each homogeneous area, and was corrected to account for the N contribution provided to the crop by organic matter mineralization. Soil property maps derived from low induction electromagnetic measurements were used to calculate N balances for a field application of VRT nitrogen fertilization. A low-induction electromagnetic mini explorer (GF Instruments Brno-CZ) was used to investigate the spatial variability of the soil. For the variable rate nitrogen treatments, the final prescription map was created using the QGIS 2.18.4 software, and N doses were applied in each homogeneous area using a Kuhn Axis-40–2-w fertilizer spreader mounted on a John Deere 6910 tractor.

LCA modeling

This LCA study was based on the LCA framework's four main phases: goal and scope definition, life cycle inventory, life cycle impact assessment, and life cycle interpretation of results.

Goal and scope

In this study, a cradle-to-farm gate LCA study was performed. Crop cultivation started with tillage for seeding; after that, seeding occurred, plant protection and fertilization were performed for crop growth, and at the last stage, harvesting took place. A flow chart of the system boundary is shown in Fig. 2. The analysis also takes into account the production of seeds, fertilizers, pesticides, fuel, tractors, and human labor within the system boundary. We distinguished foreground (direct) and background (indirect) systems when analyzing datasets. Direct field and farm emissions are substances emitted from an agricultural area or directly from the farm. In our model, we accounted for foreground emissions due to agricultural operations (fuel combustion and tyre wear), fertilizer application, and emissions of pollutants (ammonia volatilization, nitrous oxide emissions, nitrate leaching, and phosphorus compound emissions). Indirect emissions denote emissions that occur in upstream processes, such as purchased inputs used in agriculture or transportation (production of seeds, fertilizers, pesticides, fuel, lubricants, and tractor units). Both hectare (1 ha) and ton of grain (1 ton) production were used as functional units to highlight possible contrasting results on crop yield and the effect of agricultural intensification. No allocation criteria were used for allocating the impacts because it was assumed that straw was left on the field.

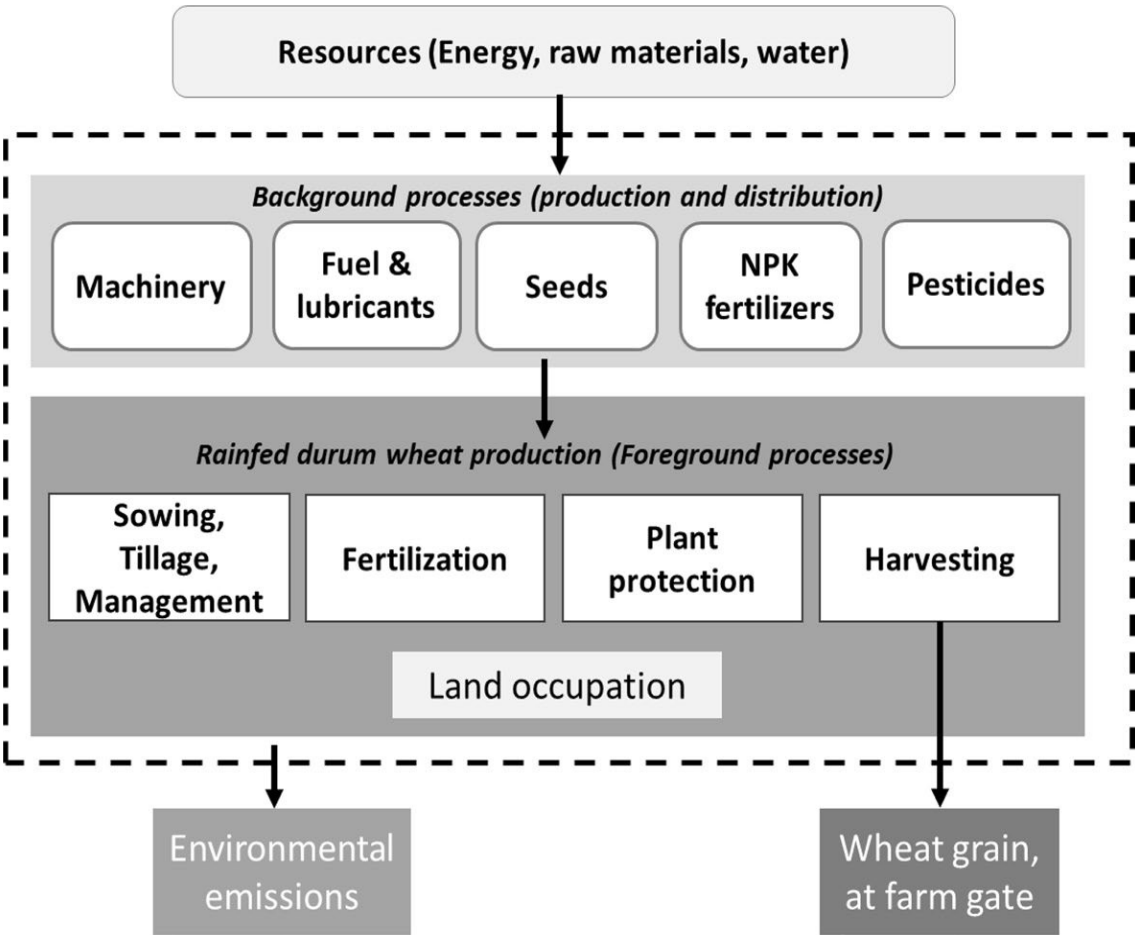


Fig. 2 *A flow chart diagram for the system boundary for wheat production*

Table 1 Inventory data for 1-ton wheat production under uniform (UA) and variable rate fertilization (VRT)

Parameter	Process modeled/Compartment	Unit	Uniform N application (UA)	Variable rate N application (VRT)
Inputs				
Seeds for sowing	Market for wheat seed, for sowing	kg t^{-1}	93.98	95.05
Nitrogen fertilizer	Market for urea, as N	kg N t^{-1}	46.1	34.82
Phosphorus fertilizer	Market for phosphate fertiliser, as P_2O_5	kg P_2O_5 t^{-1}	34.59	34.98
Pesticides, unspecified	Market for pesticide, unspecified	kg t^{-1}	0.432	0.437
Diesel fuel	Diesel, burned in building machine	MJ t^{-1}	1283	1298
Tractor machinery	Market for tractor, 4-wheel, agricultural	kg t^{-1}	3.75	3.80
Lubricating oil	Market for lubricating oil	kg t^{-1}	0.748	0.757
Land occupation	Occupation, arable, non-irrigated	m^2 t^{-1}	3383.5	3422
Human labor		h t^{-1}	3.38	3.94
Outputs				
Crop yield	Wheat grain, at the farm exit gate	t ha^{-1}	2.66	2.63
Ammonia	Emission to air, low population density	kg t^{-1}	8.39	6.35
Dinitrogen monoxide	Emission to air, low population density	kg t^{-1}	0.94	0.63
Nitrogen oxides	Emission to air, low population density	kg t^{-1}	0.15	0.12
Nitrates	Emission to water, groundwater	kg t^{-1}	40.45	7.65
Carbon dioxide, fossil	Emission to air, low population density	kg t^{-1}	72.31	54.74
Ammonia	Emission to air, low population density	kg t^{-1}	5.99E−04	6.06E−04
Benzo(a)pyrene	Emission to air, low population density	kg t^{-1}	8.99E−07	9.10E−07
Cadmium	Emission to air, low population density	kg t^{-1}	3.00E−07	3.04E−07
Carbon dioxide, fossil	Emission to air, low population density	kg t^{-1}	9.37E+01	9.47E+01
Carbon monoxide, fossil	Emission to air, low population density	kg t^{-1}	3.41E−01	3.45E−01
Chromium	Emission to air, low population density	kg t^{-1}	1.50E−06	1.52E−06
Copper	Emission to air, low population density	kg t^{-1}	5.09E−05	5.15E−05
Dinitrogen monoxide	Emission to air, low population density	kg t^{-1}	3.59E−03	3.63E−03

Table 1 (continued)

Parameter	Process modeled/Compartment	Unit	Uniform N application (UA)	Variable rate N application (VRT)
Tetrachlorodibenzo-p-dioxin	Emission to air, low population density	kg t^{-1}	1.80E−12	1.82E−12
Methane, fossil	Emission to air, low population density	kg t^{-1}	4.81E−03	4.87E−03
Nickel	Emission to air, low population density	kg t^{-1}	2.10E−06	2.13E−06
Nitrogen oxides	Emission to air, low population density	kg t^{-1}	1.32E+00	1.34E+00
NMVOC	Emission to air, low population density	kg t^{-1}	1.55E−01	1.57E−01
Polycyclic aromatic hydrocarbons	Emission to air, low population density	kg t^{-1}	1.01E−04	1.02E−04
Particulates, < 2.5 um	Emission to air, low population density	kg t^{-1}	1.21E−01	1.22E−01
Particulates, > 10 um	Emission to air, low population density	kg t^{-1}	8.06E−03	8.15E−03
Particulates, > 2.5 um, and < 10 um	Emission to air, low population density	kg t^{-1}	5.38E−03	5.44E−03
Selenium	Emission to air, low population density	kg t^{-1}	3.00E−07	3.04E−07
Sulfur dioxide	Emission to air, low population density	kg t^{-1}	3.03E−02	3.06E−02
Zinc	Emission to air, low population density	kg t^{-1}	3.00E−05	3.04E−05
Phosphate	Emission to water, groundwater	kg t^{-1}	0.1206	0.1209
Phosphorus	Emission to water, surface water	kg t^{-1}	0.636	0.644
2,4-D	Emission to soil/agricultural	kg t^{-1}	7.9E−06	5.6E−05
Chloridazon	Emission to soil/agricultural	kg t^{-1}	4.2E−06	2.9E−05
Chlormequat	Emission to soil/agricultural	kg t^{-1}	2.2E−05	1.5E−04
Choline chloride	Emission to soil/agricultural	kg t^{-1}	8.9E−06	6.2E−05
Cyprodinil	Emission to soil/agricultural	kg t^{-1}	5.6E−06	3.9E−05
Fenpropidin	Emission to soil/agricultural	kg t^{-1}	3.0E−06	2.1E−05
Glyphosate	Emission to soil/agricultural	kg t^{-1}	1.5E−05	1.1E−04
Isoproturon	Emission to soil/agricultural	kg t^{-1}	3.4E−06	2.4E−05
MCPA	Emission to soil/agricultural	kg t^{-1}	6.8E−06	4.7E−05
Mecoprop	Emission to soil/agricultural	kg t^{-1}	3.7E−06	2.6E−05

Table 1 (continued)

Parameter	Process modeled/Compartment	Unit	Uniform N application (UA)	Variable rate N application (VRT)
Metsulfuron-methyl	Emission to soil/agricultural	kg t^{-1}	7.5E−08	5.2E−07
Picoxystrobin	Emission to soil/agricultural	kg t^{-1}	1.5E−07	1.1E−06
Pyraclostrobin (prop)	Emission to soil/agricultural	kg t^{-1}	5.9E−07	4.2E−06
Bromoxynil	Emission to soil/agricultural	kg t^{-1}	6.94E−06	1.83E−05
Fluroxypyr	Emission to soil/agricultural	kg t^{-1}	7.23E−06	1.90E−05
Ioxynil	Emission to soil/agricultural	kg t^{-1}	7.09E−06	1.86E−05
Metaldehyde	Emission to soil/agricultural	kg t^{-1}	7.73E−06	2.03E−05
Propiconazole	Emission to soil/agricultural	kg t^{-1}	5.16E−06	1.36E−05

Life cycle inventory (LCI)

The primary input data are presented in Table 1. The production input data such as seed rate for sowing, plant protection product, fertilization amount and types, fuel consumption, and machinery working hours were collected at the farm during field tests and surveys. Nitrogen emissions (nitrate leaching; ammonia volatilization, and nitrous and nitrogen oxides emissions in the atmosphere), phosphate emissions in water, and fossil CO_2 to air were calculated using Koeble (2014) and Nemecek et al (2020) guidelines. N_2O emissions from atmospheric deposition of N on soils and water surfaces and emissions from N leaching and runoff were included in the indirect emissions. Direct N_2O emissions were equivalent to 1% of the amount of N applied as fertilizer (0.01 kg N_2O-N). Ammonia volatilization was considered as 0.1 kg NH_3-N/kgN. The indirect N_2O from atmospheric deposition was 0.01 kg N_2O-N/kg NH_3-N while leaching/runoff (0.0075 kg N_2O-N/kg NO_3-N). The nitrate–nitrogen leaching loss was considered 0.22 kg NO_3-N/kg N for UA and 0 for VRT. In VRT all the N given with the fertilizer was taken up by the crop, while in the case of UA 22% of the N applied was not. For urea, the emission is 1.57 kg CO_2/kg Urea-N. The secondary emission of the inputs during the production stage from raw materials including fertilizer, agrochemicals, machinery, and infrastructure production was retrieved from the Ecoinvent database (Ecoinvent Database 3.1, 2014).

Energy analysis and life cycle impact assessment

The performance assessment included energy input-output and a series of life-cycle environmental impacts. To evaluate the energy performance, various energy indices such as energy consumption, energy use efficiency (EUE), net energy gain (NEG), energy productivity (EP), and specific energy (SE) were used (Table 2). The energy input was obtained as a product of each input and its corresponding energy coefficient.

Table 2 The average value of energy equivalent coefficient of inputs and outputs

Parameter	Energy equivalents (MJ unit^{-1})	Unit	Category of input	Source of energy	References
Human labor	1.96	h	Direct	Renewable	Ilahi et al. (2019)
Seeds	13	kg	Indirect	Renewable	Ilahi et al. (2019)
Nitrogen-based fertilizers	78.1	kg	Indirect	Non-renewable	Ilahi et al. (2019)
Phosphorus based fertilizers	15.28	kg	Indirect	Non-renewable	Ilahi et al. (2019)
Pesticide, unspecified	101.2	kg	Indirect	Non-renewable	Taki et al. (2018)
Diesel fuel, tractor	47.8	kg	Direct	Non-renewable	Ilahi et al. (2019) and Taki t al. (2018)
Tractor, module manufacturing	132	kg	Indirect	Non-renewable	Ilahi et al. (2019)
Wheat, yield	13	kg	-	-	Ilahi et al. (2019)

It was classified into direct and indirect, and renewable and non-renewable. The total energy input was calculated as the sum of all energy inputs for all resources used in crop production. The output energy was obtained as a product of yield and its equivalent energy representative.

Energy use efficiency (EUE) was calculated from the ratio of energy output and energy input (Eq. 1). An increase in the ratio indicates an improvement in energy efficiency.

$$\text{Energy use efficiency} = \frac{\text{Energy output (MJ ha}^{-1}\text{)}}{\text{Energy input (MJ ha}^{-1}\text{)}} \tag{1}$$

Energy productivity (EP) was measured from the ratio of crop output of wheat and energy input (Eq. 2). An increase in the indicator denotes high EP and vice versa.

$$\text{Energy productivity (kg MJ}^{-1}\text{)} = \frac{\text{Crop output (kg ha}^{-1}\text{)}}{\text{Energy input (MJ ha}^{-1}\text{)}} \tag{2}$$

Specific energy (SE) was estimated from the ratio of energy input and crop output (Eq. 3). An increase in the indicator denotes lower energy efficiency and vice versa.

$$\text{Specific energy (MJ kg}^{-1}\text{)} = \frac{\text{Energy input (MJ ha}^{-1}\text{)}}{\text{Crop output (kg ha}^{-1}\text{)}} \tag{3}$$

Net energy gain (NEG) was approximated by the deduction of input energy from output energy (Eq. 4).

$$\text{Net energy}\left(\text{MJ ha}^{-1}\right) = \text{Energy output}\left(\text{MJ ha}^{-1}\right) - \text{Energy input}\left(\text{MJ ha}^{-1}\right) \tag{4}$$

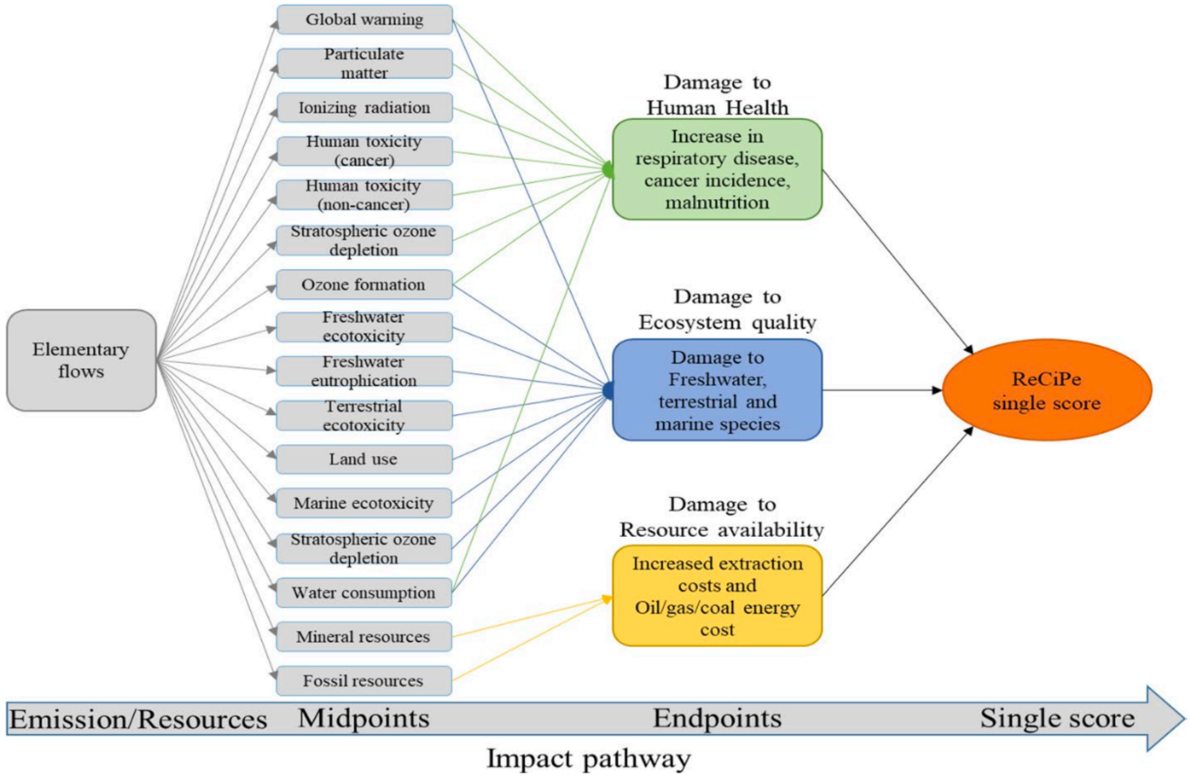


Fig. 3 ReCiPe 2016 impact pathway from inventory to aggregation to a single score

Fig. 4 Process input energy required for rainfed durum wheat production using uniform (UA) and variable rate fertilization

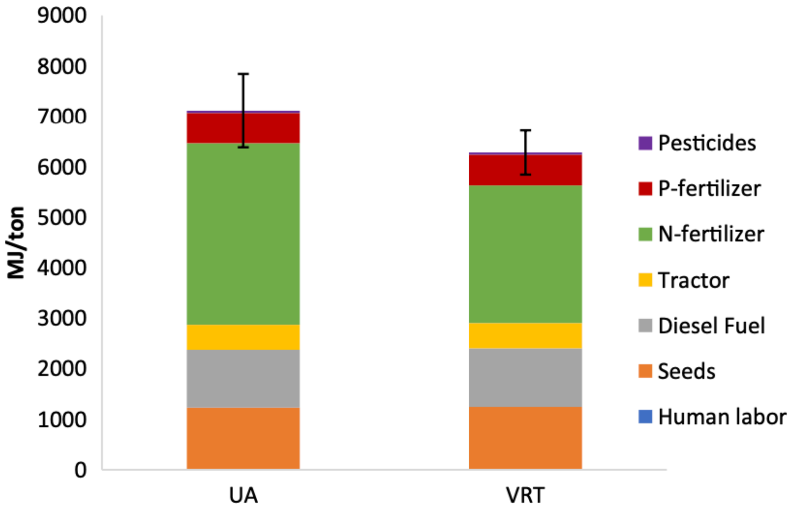


Table 3 Indicators of energy performance for wheat production with uniform (UA) and variable rate fertilization

Item	Unit	Wheat (UA)	Wheat (VRT)	Δ VRT/UA
Energy use efficiency (EUE)	–	1.83	2.07	+ 13.2%
Energy productivity (EP)	kg MJ^{-1}	0.14	0.16	+ 13.2%
Specific energy (SE)	MJ kg^{-1}	7.11	6.28	– 11.7%
Net energy gain (NEG)	MJ ha^{-1}	15 659	18 056	+ 15.3%
Direct energy (DE)	MJ ha^{-1}	1153.0	1169.1	+ 1.4%
Indirect energy (IE)	MJ ha^{-1}	5960.3	5113.7	– 14.2%
Renewable energy (RE)	MJ ha^{-1}	1229.2	1246.2	+ 1.4%
Non-renewable energy (NRE)	MJ ha^{-1}	5884.1	5036.6	– 14.4%

The life cycle impact (LCIA)-model ReCiPe 2016 (Huijbregts et al., 2017) was used to analyze environmental performance. We calculated twenty-one (21) environmental indicators (Fig. 3): eighteen (18) at the midpoint level (e.g., global warming, acidification, eutrophication, and toxicities) and three (3) at the endpoint level (human health, ecosystem quality, and resources). Midpoints were used for a more specific and detailed analysis, whereas endpoints were used to communicate the results obtained to a broader, non- expert audience. To easily compare the environmental impact of fertilization strategies, a single score index was calculated by aggregating environmental impacts into a single score expressed in a physical value (ReCiPe single score) (Fig. 3). Afterward, the computed environmental impacts were converted into externalities (environmental costs) by applying monetization weighting factors (Canaj et al., 2021). Monetizing LCA results is one way of expressing environmental impacts in terms of costs. The openLCA 1.10.3 software (https:// www.openlca.org/) was used to model the study system and to calculate the selected performance indicators. The standard deviation of the impact categories was simulated as a function of seed rate (±10%), crop yields (±10%), diesel fuel (±10%), and fertilization rates (± 10% and ± 20%).

Result and discussion

Energy performance indicators

Figure 4 and Table 3 show the results of the energy analysis for wheat production. The energy input was calculated to be 7113.3±729.3 MJ t^{-1} and 6282.8±438 MJ t^{-1} for UA and VRT, respectively. Fertilization used the most energy (Fig. 4), accounting for 59% and 53% of total energy consumption for UA and VRT, respectively. In rain-fed wheat production, chemical fertilizers are one of the top contributors to total energy consumption and environmental footprint (Canaj & Mehmeti, 2022; Ilahi et al., 2019; Taki et al., 2018).

Table 3 presents the energy use efficiency (EUE), net energy gain (NEG), energy pro- ductivity (EP), and specific energy (SE) scores. In wheat production with UA, the EUE, SE, EP, and NEG were calculated as 1.83±0.18, 7.11±0.73 MJ kg^{-1}, 0.14±0.014 kg MJ^{-1}, and 15 659 ± 3325 MJ ha^{-1}, respectively. The values for wheat with VRT were 2.07 ± 0.14, 6.28±0.44 MJ kg^{-1}, 0.16±0.011 kg MJ^{-1}, and 18 084±730.7 MJ ha^{-1}. Accordingly, VRT increased EUE and EP by 13.3%, reduced SE and total energy inputs by 11.7%, and increased NEG by 15.3%. Both systems relied on non-renewable energy sources (>80%). The fossil energy dependence was found to decrease in VRT, as the use of non-renewable energy decreased by 14.4% from 5884.1 MJ ha^{-1} to 5036.6 MJ ha^{-1}.

Our results agree with the findings of other studies (Fabiani et al., 2020; Jovaraus- kas et al., 2021; Kazlauskas et al., 2021; Scuola et al., 2017), in which VRT technology improves energy performance indicators of wheat production. Kazlauskas et al. (2021) demonstrated that using VRT technology could save 5.2% of energy input (12 059 vs. 12 726 MJ ha^{-1}) in wheat production in Lithuania. Jovarauskas et al. (2021) estimated that VRT reduced total energy input by 10.46% in Lithuanian winter wheat production, which resulted in approximately 9% higher energy efficiency (4.58 vs. 4.18) and produc- tivity (0.327±0.015 kg MJ−1 vs. 0.299±0.012 kg MJ−1). In Central Italy, Scuola et al. (2017) estimated a 30.15% (12 732 vs. 18 228 MJ) reduction in non-renewable energy con- sumption. Fabiani et al. (2020) discovered that using VRT applications in Greek wheat production could increase EUE by 14% (2.51 vs. 2.21) and decrease SE by 12% (5.7 vs. 6.56 MJ kg^{-1}) compared to the Czech Republic, where the authors estimated marginal effects with less than 2% benefits.

Environmental performance at the midpoint and endpoint level

Table 4 shows the results of impact category indicators at the midpoint level for 1 hectare and 1 ton of product. The findings show that VRT had a negligible impact on many environmental impacts (such as mineral resource scarcity, ozone formation, human toxicity, water consumption, and so on), with benefits of less than 5%. The VRT demonstrated a general reduction in potential impacts for 1 ha of wheat cultivated. For one ton of wheat, the VRT had a minor negative impact on freshwater eutrophication, freshwater, marine, and terrestrial ecotoxicity, and land use. In our study, the yield of wheat with VRT was slightly lower than in UA. Nevertheless, our model results show that the application of the VRT for a precise N-fertilization system allows reducing several environmental impacts, such as global warming (− 17.9%), fine particulate matter formation (− 19.7%), stratospheric ozone depletion (− 28.7%), terrestrial acidification (− 22.3%), and marine eutrophication (− 87.8%).

Table 4 Average cradle-to-farm gate midpoint environmental impacts of wheat production with uniform (UA) and variable rate fertilization (VRT)

Indicator	Abbreviation	Unit	1 ton			1 ha		
			UA	VRT	Δ VRT/UA	UA	VRT	Δ VRT/UA
Fine particulate matter formation	PMPF	kg PM2.5 eq	7.33	5.88	− 19.7%	19.5	15.5	− 20.6%
Fossil resource scarcity	FFP	kg oil eq	147.6	133.5	− 9.5%	392.5	351.0	− 10.6%
Freshwater ecotoxicity	FETP	kg 1,4 DCB eq	452.9	457.2	+0.9%	1204.8	1202.4	− 0.2%
Freshwater eutrophication	FEP	kg P-eq	0.29	0.30	+0.3%	0.784	0.777	− 0.8%
Global warming	GWP	kg CO_2 eq	816.3	670.2	− 18.0%	2171.39	1762.73	− 18.9%
Human carcinogenic toxicity	HTPc	kg 1,4 DCB eq	14.3	13.7	− 4.0%	38.0	36.0	− 5.1%
Human non—carcinogenic toxicity	HTPnc	kg 1,4 DCB eq	483.3	465.4	− 3.7%	1285.6	1223.9	− 4.8%
Ionizing radiation	IRP	kBq Co-60 eq	40.1	38.9	− 3.1%	106.7	102.2	− 4.2%
Land use	LU	m^2a crop eq	7056.5	7136.6	+1.1%	18 770.27	18 769.30	− 0.01%
Marine ecotoxicity	METP	kg 1,4 DCB-eq	691.7	698.2	+0.9%	1839.91	1836.31	− 0.2%
Marine eutrophication	MEP	kg N eq	3.1	0.4	− 87.8%	8.23	0.99	− 88.0%
Mineral resource scarcity	MRS	kg Cu eq	6.49	6.37	− 1.9%	17.3	16.7	− 3.0%
Human health ozone formation	HOFP	kg NOx eq	2.76	2.68	− 3.1%	7.35	7.04	− 4.2%
Ecosystem ozone formation	EOFP	kg NOx eq	6.32	6.12	− 3.2%	16.8	16.1	− 4.3%
Stratospheric ozone depletion	ODP	kg CFC11 eq	0.0119	0.01	− 28.7%	0.03	0.02	− 29.5%
Terrestrial acidification	TAP	kg SO_2 eq	45.36	35.26	− 22.3%	120.7	92.7	− 23.2%
Terrestrial ecotoxicity	TETP	kg 1,4 DCB-eq	72 430	73 040	+0.8%	192 664	192 096	− 0.3%
Water consumption	WCP	m^3 consumed	45.3	43.7	− 3.7%	120.6	114.8	− 4.8%

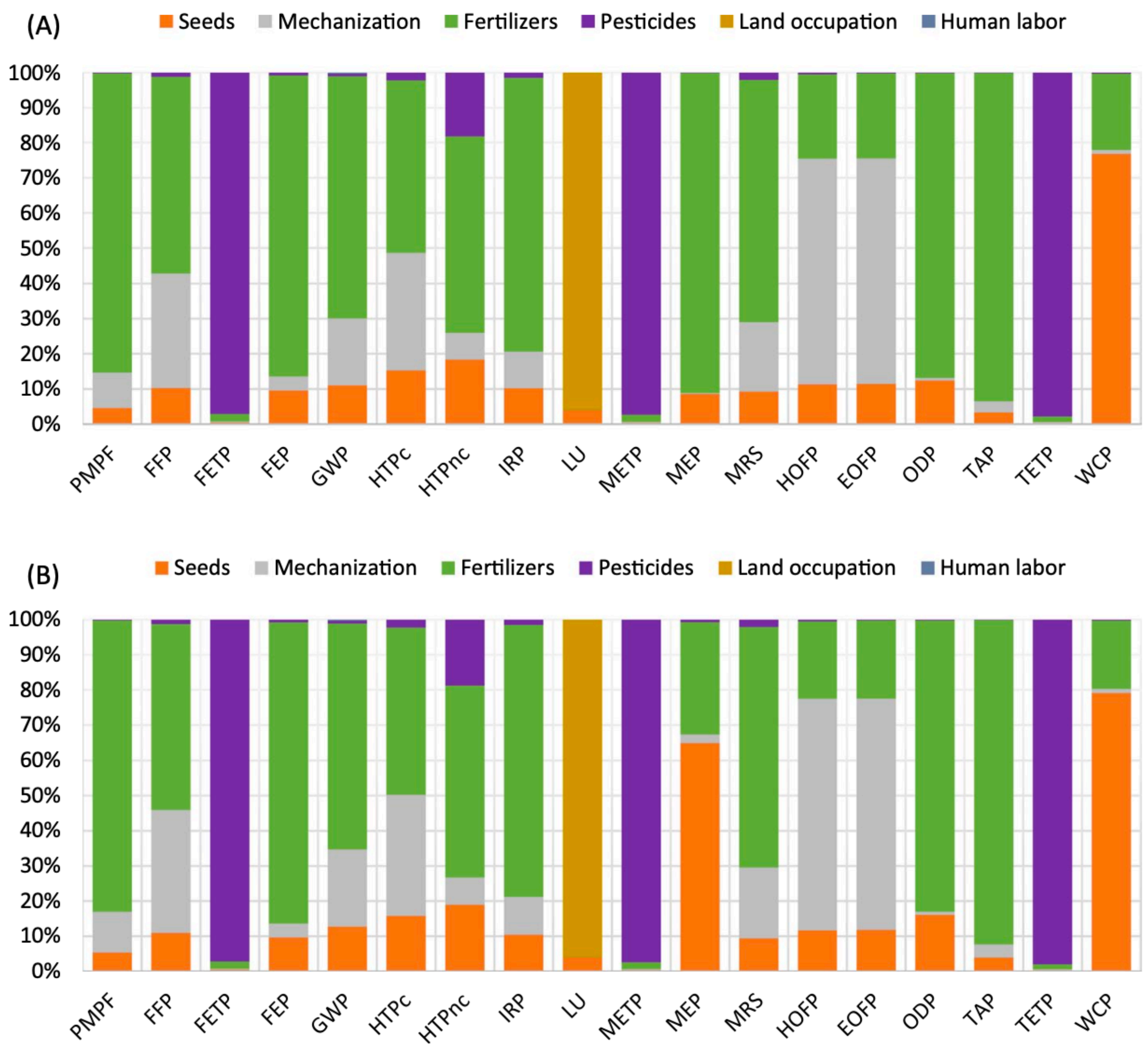


Fig. 5 Contribution of agricultural inputs and processes to the environmental impacts of wheat production: **A** UA, **B** VRT

These environmental impacts were mitigated by reducing on-farm (foreground) emissions. The higher land application of N compounds as chemical fertilizers had a negative influence on the environment through the release of N-containing gases such as NH_3 and N_2O, and nitrate (NO_3^-) losses via leaching and runoff. Further, the use of every kg of urea essentially induces CO_2 emissions after its usage. The reduction of soil N_2O emissions and CO_2 releases after urea applications reduced global warming. Reduction of ammonia (NH_3) volatilization and nitrogen oxide (NOx) emissions had the greatest impact on fine particulate matter formation and terrestrial acidification. Marine eutrophication occurred due to the nitrate originating from agricultural runoff and leaching (water- borne N-emissions).

The relative contribution of the agricultural inputs to the environmental impacts of wheat is presented in Fig. 5. For both UA and VRT, fertilizers had the greatest environmental impact (12 out of 18). Photochemical ozone formation was greatly affected by mechanized field operations (i.e., diesel fuel emissions), whereas pesticide use caused freshwater, marine, and terrestrial ecotoxicity. The greatest impact on water consumption was caused by seed production.

Figure 6 depicts the numerical endpoint scores for 1 ton of product. The benefits of VRT to areas of protection (human health, ecosystems, and resources) ranged from 3.3% to 13.5% for 1 ton of product and from 4.4% to 14.2% for 1 ha of land. For UA, the damage to human health, ecosystem quality, and resource availability was 9.43E−03±9.77E−04 DALY t^{-1}, 4.15E−05±4.6E−06 species.yr t^{-1} and 58.28±6.53 USD2013 t^{-1}, respectively. For VRT, the damage to human health, ecosystem quality, and resource availability was 8.16E−03±5.52E−04 DALY t^{-1}, 4.01E−05±1.9E−06 species.yr t^{-1} and 52.9±2.9 USD2013 t^{-1}, respectively. The aggregation of the weighted results into a single score showed that damage to human health is controlled by fine particulate matter formation, which is due to the volatilization of ammonia (NH_3). In terms of ecosystem quality, agricultural land occupation accounted for more than 47% of the footprint. The scarcity of fossil fuels is the primary determinant of resource availability.

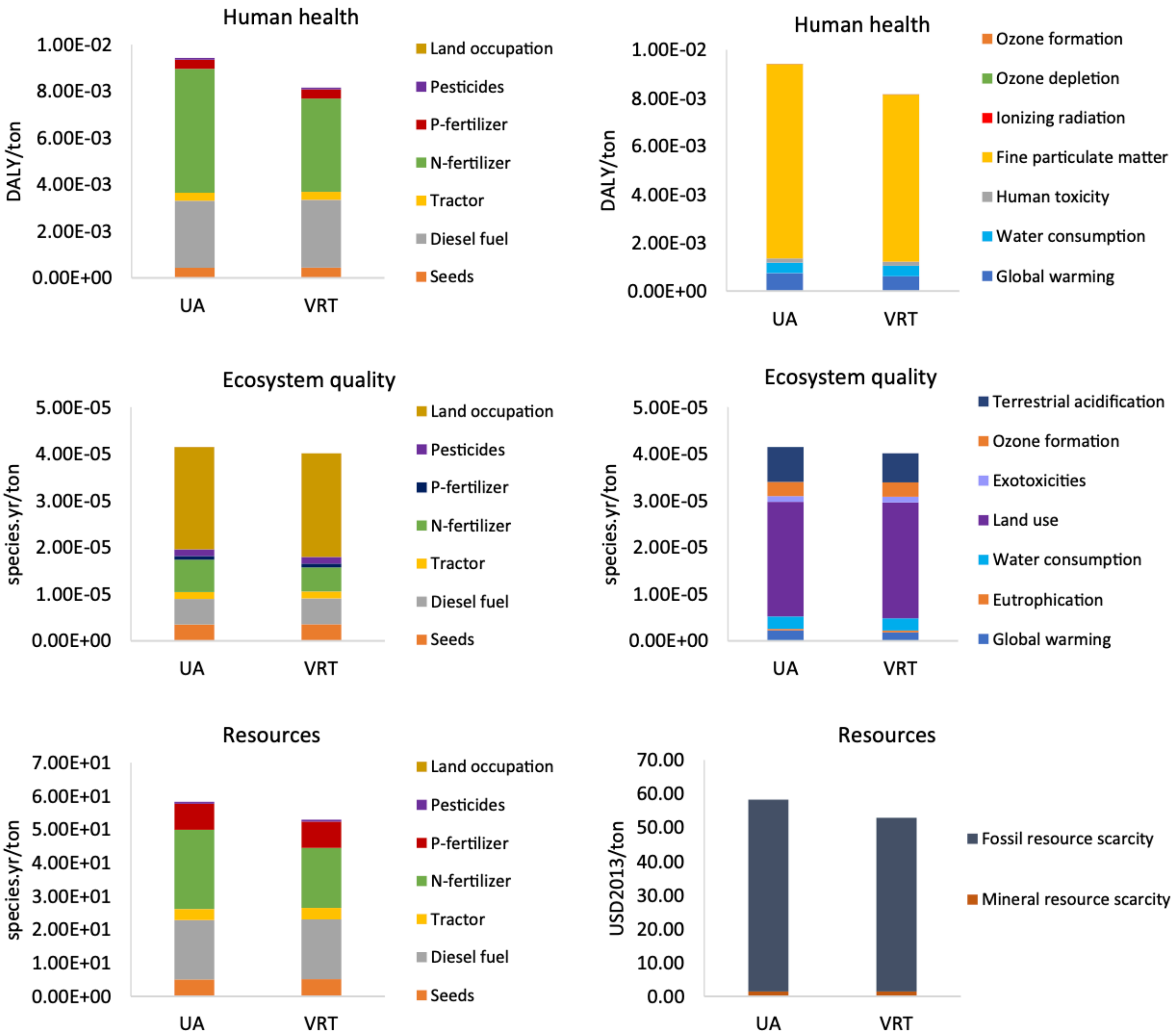


Fig. 6 Scores for human health, ecosystem quality, and resource availability in wheat production using uniform (UA) and variable rate fertilization (VRT), with input/process and indicator contributions

LCA single score analysis (physical weighting)

Figure 7 depicts the aggregated single-score indicator, expressed as a physical value (ReCiPe single score). Wheat production with UA and VRT was estimated to have an environ- mental footprint of 182.3±18.8 and 160.1±11.2 points ton^{-1} respectively. The footprint for 1 ha was 484.9 ± 49.9 points and 421.1 ± 29.4 points for UA and VRT, respectively.

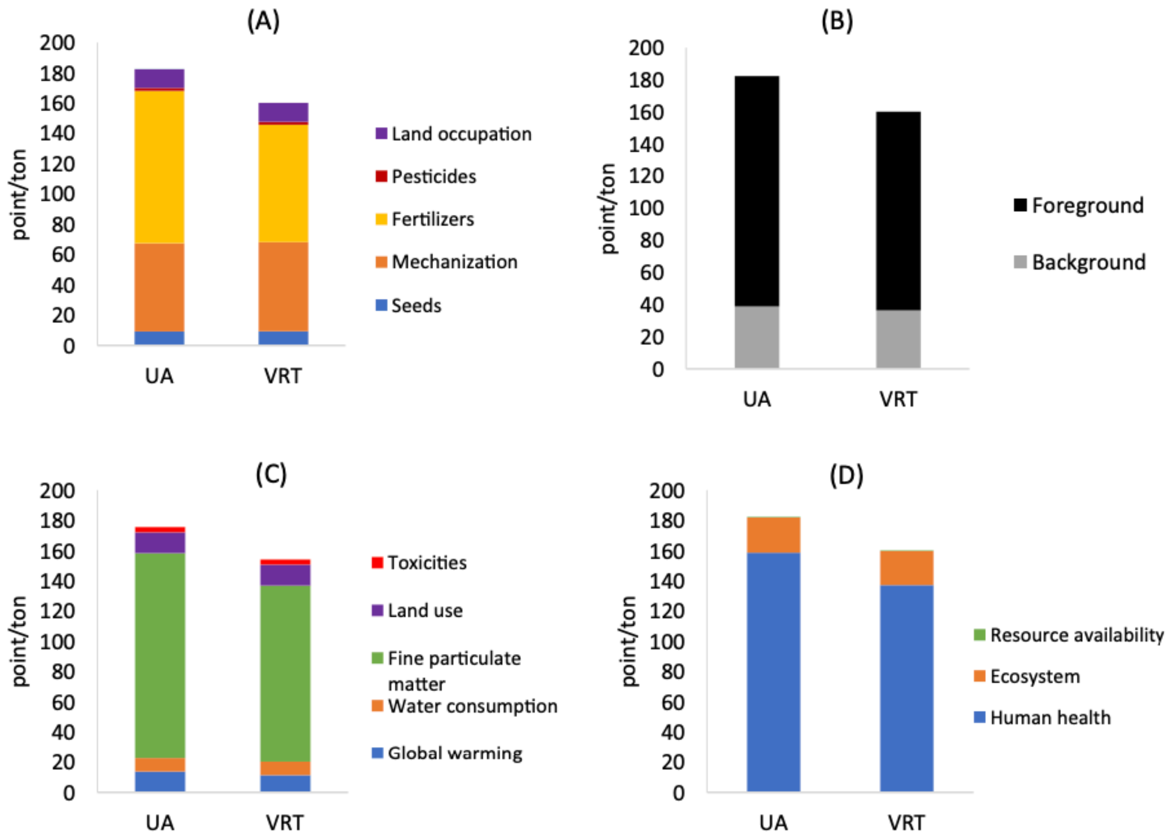
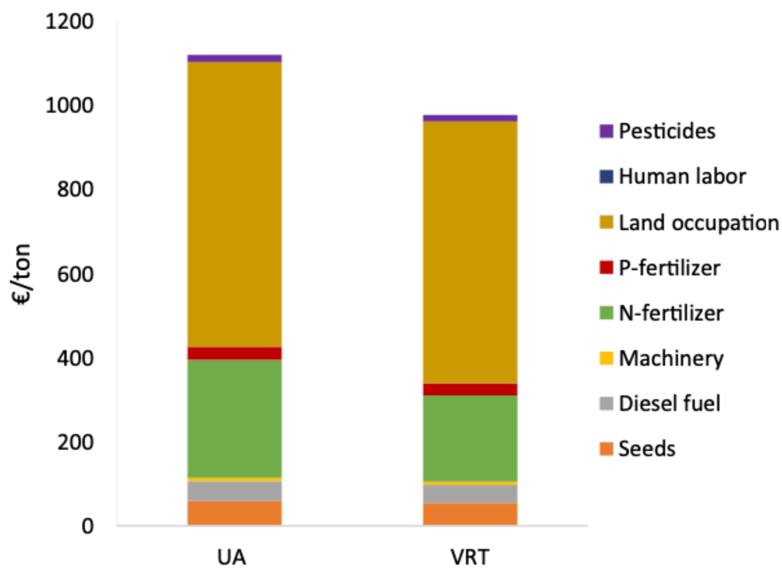


Fig. 7 Single score environmental impact of wheat production with uniform (UA) and variable rate fertilization (VRT). **A** Process contribution; **B** Subsystem contribution; **C** Midpoint impact contribution; **D** Endpoint impact contribution

Fig. 8 The external environmental cost of wheat production under uniform (UA) and variable rate fertilization (VRT)



With VRT, the fertilization environmental footprint of wheat production was reduced by 23%, from 100.7 points per ton to 77.6 points per ton. Considering the cradle-to-farm gate perspective, VRT could reduce the total environmental footprint by 12.2% per ton of product or 13.1% per hectare cultivated. The background subsystem (production and trans- port of N-fertilizers) was responsible for about 6% of the reduction, while the foreground subsystem was responsible for 14% (application of N-fertilizers). The highest benefits were due to the reduction of fine particulate matter formation as a result of NH_3 reduction.

LCA single score analysis (external environmental cost)

Figure 8 depicts the aggregated single-score indicator, which is expressed in monetary value (EURO) and represents the external environmental cost. Wheat production with UA and VRT has external environmental costs of 1151.3 ± 80.4 and 1075.2 ± 73.2 Euros ton^{-1}, respectively. Considering the cradle-to-farm gate perspective, wheat with VRT can reduce the external environmental cost by 6.6% for 1 ton of product and 7.7% for 1 ha of land. Differently from physical weighting, money gives more value to land occupation, an indicator that is related mainly to crop yield and no farm inputs. Production of wheat crops needs adequate land requirements (Romano et al., 2021). Land use is the main driver of global biodiversity loss, and its environmental relevance is widely recognized in research on LCA (De Baan et al., 2013), as there are external costs associated with biodiversity loss associated with land use (De Bruyn et al., 2018). The economic analysis literature indicates that the production costs of wheat production in southern Italian regions were 992 EUR ha^{-1}(Pazienza & Zanni, 2009), 512.52 to 693.96 EUR ha^{-1} (Tiberti, 2013), 379 and 784.1 EUR ha^{-1} (Todorović et al., 2018) and 926.5 to 1023.8 EUR ha^{-1} (Bux et al., 2022). These figures show that indirect costs can be as high as or higher than production costs. This confirms that the true cost performance of variable rate technology will be greatly under- estimated if the environmental cost is not considered. Environmental impact monetization could be considered in cost–benefit analyses as a further evaluation attempt.

Comparison of our findings with other studies

Several LCA studies on wheat production have been conducted, but with a limited focus on the benefits of variable fertilization (Jovarauskas et al., 2021; Kazlauskas et al., 2021; Medel-Jiménez et al., 2022; Scuola et al., 2017). As a result, we provided an overview and compare findings with other several other LCA studies on variable rate fertilization that have been published internationally (Table 5). Jovarauskas et al. (2021) and Kazlauskas et al. (2021) found that variable-rate fertilization on wheat production could reduce the GHG emissions by 5.2% to 9.5%. Scuola et al. (2017) estimated a 32% lower carbon footprint in the cultivation of bread wheat through precision agriculture in Central Italy. Further reductions were estimated for blue water, acidification, and eutrophication potential. Medel-Jiménez et al. (2022) estimated an 8.6% reduction in the climate change impact by using the ground-based optical crop sensor for variable rate nitrogen application in Austrian conditions. Other remarkable benefits were observed for freshwater eutrophication (− 21.23%), human toxicity (− 20.20%), and marine eutrophication (− 9.05%). According to Van Der Laan et al. (2015), total energy input and GHG emissions in sugarcane production in Brazil could be cut by 20% and 25%, respectively. According to Li et al. (2016), sensor-based nitrogen application in corn production in the USA could reduce life cycle non-renewable energy consumption, global warming, acidification potential, and eutrophication potential by 7, 10, 22, and 16%, respectively. Variable rate nutrient application, according to Balafoutis et al. (2017), could reduce the carbon footprint of the vineyard in Northern Greece by 28.3% when compared to conventional production. Vatsanidou et al. (2020) demonstrated the environmental benefit of variable rate fertilization by reducing air emissions from fertilizer application in pear orchards in Greece by nearly 50%. Variable-rate fertilization could reduce the environmental impact of rice production in Italy by up to 13.6% when compared to uniform N application (Bacenetti et al., 2020). Meza-Palacios et al. (2020) showed that a decision support system for NPK fertilization in sugarcane farms could reduce on average damage to human health by 11%, damage to ecosystem quality by 9%, climate change impact by 14.5%, and resource availability by 11.5%. Sanches et al. (2021) estimated that applying fertilizer at variable rates in sugarcane production could reduce climate change by 3.4% and fossil fuel depletion by 4.2% per ton of product. According to Núñez-Cárdenas et al. (2022), using precision agriculture practices in Spanish conditions could reduce the carbon footprint of nectarine production per kg of fresh fruit at the farm's gate by 20.5%. Casson et al. (2022) found that variable-rate drip irrigation and fertigation in Italian grape farms can significantly reduce the CO_2-eq emissions generated during grape production by over 50%. In general, the majority of LCA studies show that variable-rate fertilizer application has environmental benefits. These benefits of VRT technology vary from study to study depending on data availability and accuracy, system boundaries, modeling approach, functional unit, and life cycle impact assessment method. Future case studies are thus required to test new indicators, new LCIA methods, and their outcomes.

Table 5 Literature LCA studies on variable rate fertilization

Author	Geographical scope	Crop	Main findings on precision agriculture/variable rate fertilization
Van Der Laan et al. (2015)	Brazil	Sugarcane	VRA reduced energy input by 20% and GHG by 25%
Li et al. (2016)	USA	Corn	Precision application of N is predicted to have reduced soil NO emissions by 10%, volatilized NH loss by 23%, and NO leaching by 16%, which in turn reduced life cycle nonrenewable energy consumption, GWP, acidification potential, and eutrophication potential by 7, 10, 22, and 16%, respectively
van Evert et al. (2017)	Greece and Netherlands	Olive	Variable rate application for side-dress N (SN) can lead to a reduction of nitrogen fertilizer use of 15%. The externality of GHG emissions is reduced from 136 € ha^{-1} to 124 € ha^{-1} (a 9% reduction). VRA for SN also reduces eutrophication by 17%
Balafoutis et al. (2017)	Greece	Vineyard	Precision viticulture led to a PCF reduction of 28.3% compared to conventional production
Scuola et al. (2017)	Italy	Bread wheat (Triticum aestivum L.)	Precision agriculture under integrated farming (IFPA) in the cultivation of bread wheat (Triticum aestivum L.) improved global warming, blue water, non-renewable energy consumption, acidification, and eutrophication potential
Vatsanidou et al. (2020)	Greece	Pear Orchard	The environmental benefit of using the variable rate fertilization with a reduction of almost 50% of air emissions from fertilizer application in pear orchards
Bacenetti et al. (2020)	Italy	Paddy rice	Variable-rate fertilization allowed for reducing the environmental impact by 11.0% to 13.6% as compared to uniform N application
Meza-Palacios et al. (2020)	Mexico	Sugarcane	The decision support system for NPK fertilization could reduce on average damage to human health by 11%, damage to ecosystem quality by 9%, climate change impact by 14.5%, and resources by 11.5%
Núñez-Cárdenas et al. (2022)	Spain	Nectarine	Variable rate drip irrigation and fertigation can significantly reduce the CO_2 equivalent emissions generated during grape production by over 50% and increase water use efficiency by over 30% (for traditional nutrient and water management)
Casson et al. (2022)	Italy	Vineyards	Variable rate drip irrigation and fertigation can significantly reduce the CO_2 equivalent emissions generated during grape production by over 50%
Sanches et al. (2021)	Brazil	Sugarcane	N and P applications were reduced using VRT, allowing the production of a similar yield with the saving of inputs
Jovarauskas et al. (2021)	Lithuania	Wheat	GHG emissions were 9.4% lower than when variable rate fertilization was used
Kazlauskas et al. (2021)	Lithuania	Wheat	Variable rate fertilization on wheat production allowed reducing the GHG emissions by 5.2%

Table 5 (continued)

Author	Geographical scope	Crop	Main findings on precision agriculture/variable rate fertilization
Medel-Jiménez et al. (2022)	Austria	Wheat	A crop sensor for nitrogen fertilization could reduce the global warming potential of fertilization by 8.6%, freshwater eutrophication by 21.23%), human toxicity by 20.20%, and marine eutrophication (-by 9.05%)

Discussion

Fertilization is an essential crop input for wheat production; however, improper N application rates can result in serious environmental concerns from fertilizer production and application. Precision farming has been widely expected to show environmental benefits; however, the magnitudes of these effects are largely uncertain and case-dependent (Finger et al., 2019). Here, using a multi-indicator life cycle impact assessment model, we compared the energy and environmental impacts of wheat production under uniform and variable rate fertilization strategies. VRT resulted in a 25% reduction in nitrogen fertilizer with the same level of yield as UA. This level of nitrogen efficiency provided environmental benefits on air-related environmental indicators of particulate matter formation, global warming, and terrestrial acidification, which depended on emissions of ammonia (NH_3), nitrogen oxide (NOx), and nitrous oxide (N_2O). Our model results showed that the reduction of NH_3 had a greater influence on the final environmental benefits of wheat production. Similar previous findings (Medel-Jiménez et al., 2022) have revealed that the amount of applied N fertilizer has a greater influence on NH_3 and NO_3 indirect soil emissions than on direct N_2O emissions. Fine particulate matter formation is an indicator of air pollution that causes primary and secondary aerosols in the atmosphere and can have a substantial negative impact on human health (Huijbregts et al., 2017). For some environmental impacts, a minor negative effect was observed due to the effect of crop yield. According to the single-score analysis, wheat production with VRT has lower pollution-related environ- mental impacts per unit of product and land area. The findings, which are consistent with previous energy-related (Fabiani et al., 2020; Jovarauskas et al., 2021; Scuola et al., 2017) and LCA research (Bacenetti et al., 2020; Medel-Jiménez et al., 2022; Vatsanidou et al., 2020), highlight the value of VRT in input management to reduce nitrogen application rates while maintaining crop productivity and providing energy as well as numerous environmental benefits. Yet, our study highlighted that the overall expected benefits of smart agricultural technologies in annual crops are not always straightforward due to trade-offs between environmental indicators. In this study, land-use impacts that are not controlled by crop yield rather than fertilization had a significant effect on the overall co-benefits or co-damages of wheat production. This suggests that the consideration of multiple metrics needs to simultaneously explore trade-offs that may exist between productivity and environmental sustainability. Higher grain yields are expected to have a lower impact on land occupation; thus, the environmental benefits of VRT could be maximized by simultaneously increasing grain yield and optimizing the fertilizer rates. Understanding the spatial and temporal interactions between soil–plant-atmosphere is required for the successful implementation of site-specific N management (Basso et al., 2016). It is demonstrated that soil type, meteorological conditions, and N fertilizer rate and type have significant implications for N availability and crop uptake (Pampana & Mariotti, 2021) and crop yield, energy performance, and economic efficiency (Jovarauskas et al., 2021). Therefore, to realize the full potential of VRT, weather, soil, and landscape data should be combined when implementing variable rate treatments.

The decision to use variable rate fertilization would be based on economic performance. Until now, literature has produced contradictory results on the profitability of such concept. Farm sizes and the level of efficiency of the “business-as-usual scenario” influence the eco- nomic impact of the VRT (Fabiani et al., 2020). To be profitable, variable rate N management must accurately match N requirements to crop N demands (Long et al., 2015). Even with an increase in yield and cost savings on crop production inputs, using VRT technology may result in high costs, especially in small-scale farming systems (Späti et al., 2021). For the first time, this paper introduces the concept of monetization life-cycle assessment results to estimate the indirect cost of wheat production under the precision management of fertilizers. Our research found that VRT can have indirect economic benefits because the indirect costs (environmental externalities as external costs) are lower than with uniform management. Thus, we emphasize that a more comprehensive LCA that includes these environmental impact monetizations is required to investigate the “true cost” performance of VRT by quantifying the cost of environmental impacts and directly integrating them with economic costs.

Conclusion

This study used a multi-indicator model and lifecycle-based indicators to compare the performance of rainfed wheat production using uniform (UA) and variable N fertilization (VRT). According to our model results, the VRT can reduce indirect energy inputs while increasing energy efficiency and productivity by at least 10%. The LCA findings show that there is a range of potential environmental benefits associated with VRT on wheat cultivation, including reductions in global warming, fine particulate matter formation, stratospheric ozone depletion, terrestrial acidification, and marine eutrophication. Our model indicated that fertilizer use efficiency drives on-farm environmental benefits (reduction of N losses due to leaching, denitrification, ammonia volatilization, and fossil CO_2 emissions) more than indirect benefits (emissions that come from the manufacture of synthetic N fertilizer). Aggregating the results into a single score demonstrated that physical environ- mental benefits can be up to 12.2% and indirect economic benefits (hidden environmental costs) can be up to 7.7%. These results outline that VRT is a promising option for sustain- able extensification and improved eco-efficiency of wheat production in a Mediterranean context.

As a result of our research, we conclude that for annual crops, multiple metrics need to be considered to explore the full range of trade-offs and synergies between different environmental indicators. The analysis shall include mass-based and land-use-based functional units to capture trade-offs between environmental performance, land use, and productivity. It is necessary to improve the methodology by combining life cycle assessment, monetization, and life cycle costing to explore the connection between direct and indirect financial implications and environmental benefits in a life cycle context. This would be a great step for the to support decision-making regarding the “true” sustainability of VRT.

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Chapter 4. Uptake and accumulation of emerging contaminants in processing tomato irrigated with tertiary treated wastewater effluent: a pilot-scale study.

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Abstract

The reuse of treated wastewater for crop irrigation is vital in water-scarce semi- arid regions. However, concerns arise regarding emerging contaminants (ECs) that persist in treated wastewater and may accumulate in irrigated crops, potentially entering the food chain and the environment. This pilot-scale study conducted in southern Italy focused on tomato plants (*Solanum lycopersicum* L. cv Taylor F1) irrigated with treated wastewater to investigate EC uptake, accumulation, and translocation processes. The experiment spanned from June to September 2021 and involved three irrigation strategies: conventional water (FW), treated wastewater spiked with 10 target contaminants at the European average dose (TWWx1), and tertiary WWTP effluent spiked with the target contaminants at a triple dose (TWWx3). The results showed distinct behaviour and distribution of ECs between the TWWx1 and TWWx3 strategies. In the TWWx3 strategy, clarithromycin, carbamazepine, metoprolol, fluconazole, and climbazole exhibited interactions with the soil-plant system, with varying degradation rates, soil accumulation rates, and plant accumulation rates. In contrast, naproxen, ketoprofen, diclofenac, sulfamethoxazole, and trimethoprim showed degradation. These findings imply that some ECs may be actively taken up by plants, potentially introducing them into the food chain and raising concerns for humans and the environment.

keywords

emerging contaminants (EC), wastewater irrigation, water reuse, plant uptake, tomato, soil contamination

Introduction

Globally, 70% of freshwater is used for agriculture, with substantially greater figures in developing countries. Agricultural water scarcity will intensify on more than 80% of global croplands (Liu et al., 2022). Meanwhile, population expansion, fast urbanization, and climate change all exacerbate water demand, resource depletion, and water pollution (Boretti and Rosa, 2019). Irrigation management is frequently complicated in water-stressed regions. The economy, crop patterns, output, food demand, and consumption will all be impacted in various ways by climate change and water scarcity (Zingaretti et al., 2013). To ensure water resources' sustainability, non-conventional water resources are becoming a reality (Chen et al., 2021). Municipal treated wastewater (hereafter referred to as reclaimed water) is increasingly being used in arid and semi-arid regions as a major alternative source of irrigation water (Ungureanu et al., 2020). Irrigation with treated wastewater has long been practiced in the Mediterranean basin, particularly in water-scarce regions where treated wastewater reuse accounts for up to 5-12% of total treated wastewater effluent. By 2021, about 44 nations used daily treated wastewater for agricultural irrigation (Hashem and Qi, 2021). The Middle East and North Africa (15%) and Western Europe (16%) have exceptionally high rates of treated wastewater reuse (Jones et al., 2021).

Reusing treated wastewater for irrigation offers numerous benefits, such as increased profitability for farmers, reduced need for expensive fertilizers due to nutrient-rich water, and preservation of freshwater resources. However, it also poses challenges related to soil salinity, human health risks from pathogens and heavy metals, and social and economic considerations. In recent years, there has been increasing concern about the environmental concerns posed by

so-called "emerging contaminants" (Taheran et al., 2018). The ECs are predominantly unregulated anthropogenic chemicals that occur in trace concentrations in air, soil, water, food, and human and animal tissues (Rout et al., 2021). Following uptake into edible plant parts, EOCs may eventually enter in the food chain, with associated human exposure (González Garcıá et al., 2019). Irrigation water (Shi et al., 2022), irrigated soils (Rogowska et al., 2020), marketed crops (Ben Mordechay et al., 2021), and even biological samples such as human urine (Schapira et al., 2020) have been found to contain ECs. Once in the soil, the ECs go through several processes that determine their fate: sorption-desorption, transport, biotic and/or abiotic transformation, and plant uptake. Lipophilicity, size, H-bond donors/acceptors moieties, and charge of ECs all influence their sorption attraction to soil particles (Gworek et al., 2021; Strawn, 2021). Soil properties, specifically soil organic matter content, pH, clay content, and clay type, also influence this process (Fu et al., 2016; De Mastro et al., 2022a). Desorption (the return of an adsorbed fraction to the soil solution) is a governing factor, particularly during the rainy season, because rainwater contains negligible concentrations of ECs, altering the EC sorption equilibrium in the soil (Ben Mordechay et al., 2022). While easily degraded ECs are transformed and/or metabolized during wastewater treatment, more persistent ECs remain in the effluents and may accumulate in soils and be taken up by plants (Ben Mordechay et al., 2018).

By implementing appropriate treatment technologies, monitoring soil and water quality, and employing careful irrigation practices, wastewater irrigation can be a safe and effective solution to address water scarcity and promote sustainable agriculture (Mishra et al., 2023). Scientific studies have attempted to characterize the uptake of EC from reclaimed water into different crops such as tomatoes (Christou et al., 2017), strawberries, and lettuce (Hyland et al., 2015; González Garcıá et al., 2019; Sunyer-Caldú et al., 2022), some common vegetables such as carrot, radish, spinach, and artichoke (Hussain et al., 2019; Beltrán et al., 2020; De Mastro et al., 2023), and others such as cucumber, eggplant, long bean, and wheat (Liu et al., 2020). The bioaccumulation factor range of ECs is normally rather extensive, depending on the examined plant, exposure length, soil qualities, climate conditions, particularly temperature and humidity, and, most crucially, the molecule's physicochemical features (Ben Mordechay et al., 2018). Yet, the synergistic effects of multiple contaminants on soil and crops are poorly understood (Lyu et al., 2022).

This study aimed to investigate the occurrence and fate of emerging contaminants (pharmaceuticals) in soil and (*Solanum lycopersicum* L.) tomato plants irrigated with municipal treated wastewater in Southern Italy. A field experiment was designed with tomato plants grown in lysimeters and subjected to freshwater and contaminated wastewater irrigation treatments. The study uses lysimeters in an open field rather than a greenhouse to closely simulate real agricultural settings, yielding insights for extrapolation studies in wastewater-related research. Furthermore, the study adds new realistic evidence on the levels of emerging contaminants in tomatoes grown on soil (lysimeters) media irrigated with fresh and treated wastewater, as well as useful information on the distribution of emerging contaminants tailored to the needs of Mediterranean environments.

Materials and methods

Experimental design and data collection

The experimental study (Figure 1) was conducted at the ALSIA Metapontum Agrobios Research Center in the province of Matera (N 40° 23', E 16° 47'), Italy, in 2021. The region has a Mediterranean climate with moderate, humid winters and hot, dry summers. During the summer months (June to September), the average temperature ranges from 24°C to 28°C. Maximum temperatures at the experimental site exceeded 30°C for days (July: 27 days, August: 31 days, September: 25 days). Winter temperatures (December to February) average between 5°C and 11°C. The annual average precipitation is around 600-700 millimeters, with the majority falling from November to April.

On 17/06/2021, the tomato cultivar 'Taylor F1' (*Solanum lycopersicum* L.; formerly Lycopersicon esculentum Mill.) was transplanted in weighing lysimeters (Figure 2).

Pre-cultivated tomato seedlings in 180-hole polystyrene honeycomb containers were transplanted into 0.8 m3 tanks at the 3rd-4th true leaf stage for each experimental treatment distributed according to the randomized block experimental scheme with four (4) repetitions (Figure 3). The experimental design entailed comparing three irrigation treatments:

i) irrigated with surface freshwater (FW) as control, obtained from the irrigation network system that is normally used by the farmers in the area for crop irrigation;

ii) irrigation with tertiary (TWW) municipal wastewater spiked with the addition of target contaminants in a dose comparable to the European average concentration (TWWx1);

iii) irrigation with tertiary (TWW) municipal wastewater spiked with emerging contaminants in a triple dose (TWWx3).

TWW effluent from a standard municipal wastewater treatment plant (WWTP) at the experimental site (Ferrandina, Italy) was utilized to determine TWWx1 and TWWx3 irrigation treatments. Rapid sand filtration (rSF) and UV treatment are used for tertiary treatment and disinfection. The experimental design includes four lysimetric measures (plots) for each irrigation treatment.

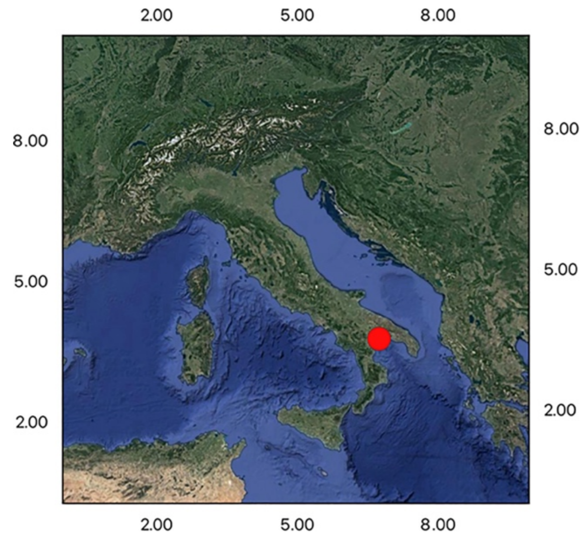


FIGURE 1

Map of Italy and location of experimental site.

FIGURE 2

Schematic representation of the lysimetric weighing system, for determining water consumption, water flow, and mass balance of ECs.

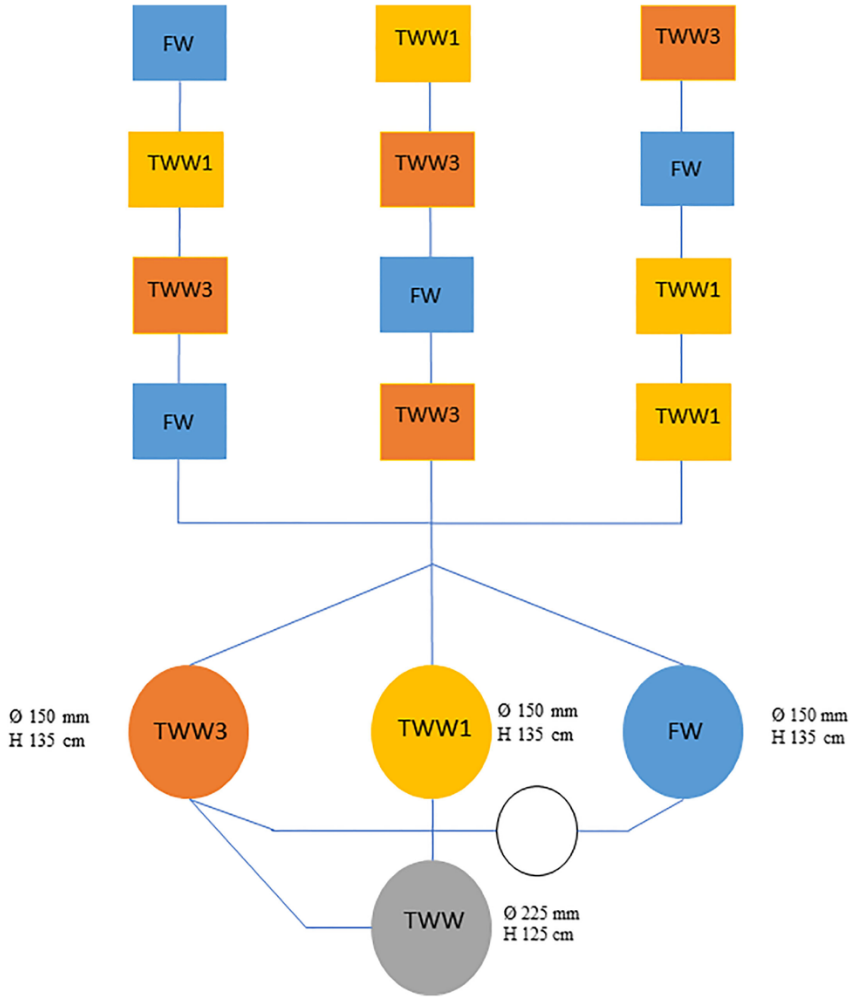


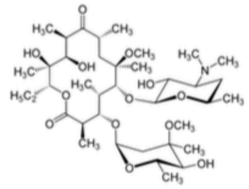
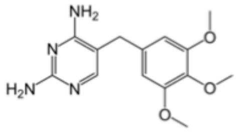
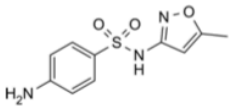
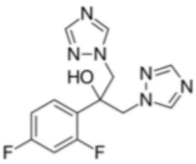
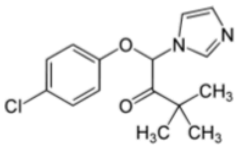
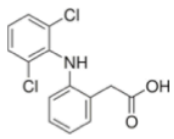
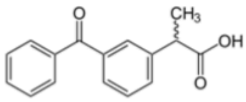
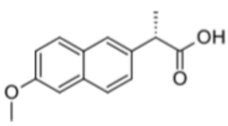
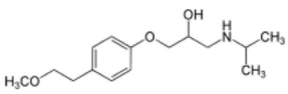
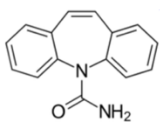
FIGURE 3
Detail of the experimental scheme (rectangles - tanks in which the treatments were prepared; red - randomized lysimeters; circle - tanks used for the storage of the treated water and its safe disposal).

Among the ECs were clarithromycin, sulfamethoxazole, trimethoprim, carbamazepine, diclofenac, fluconazole, climbazole, ketoprofene, metoprolol, and naproxen. These substances were specifically chosen due to their prevalence in wastewater; they are often not completely eradicated during standard treatments. Table 1 lists the chemical structures and attributes of the selected ECs. The concentration of these EC in treated wastewater ranged from low ng L−1 to low µg L−1 (Ben Mordechay et al., 2021). Standards (> 98% of purity) were used to prepare the multi-compound stock standard solution (1000 ppm). This solution was added to wastewater used for irrigation to achieve the concentration of 200 and 600 mg L−1 of each compound and obtain TWWx1 and TWWx3.

The lysimetric tanks were filled with sandy loams soil (United States Department of Agriculture classification) with the following physical and chemical properties: sand, 84.7%; silt, 3.3%; clay, 12.0%; field capacity (measured by pressure plate apparatus at -0.03 MPa) of 13.2% dry weight (dw); wilting point (measured by pressure plate apparatus at -1.5 MPa) of 7.2% dw, and a bulk density of 1.45 Mg m-3; pH 8.3; electrical conductivity, 0.10 dS m−1; organic matter, 0.32% (Walkley and Black method);

available phosphorus (Olsen method), 35.6 mg kg-1; total potassium, 0.92 g kg-1 (determined by coupled plasma optical emission spectrometer, Agilent, ICP-OES 720); total nitrogen, 0.51% (Kjeldahl method); mineral NO_3-N, 0,7 mg kg^{-1} ; mineral NH_4-N, 2.7 mg kg^{-1} . This type of soil is characteristic of the Ionian-Metapontine coastline and is extensively employed for vegetable cultivation (Candido et al., 2013). Additionally, this soil has allowed us to operate under favorable hydraulic conductivity conditions, enabling the monitoring of the solution's movement circulating in the soil through the use of moisture sensors. Three plants were transplanted into each tank, and throughout the cultivation cycle, typical agronomic practices for growing and processing tomatoes in Basilicata were followed. Each lysimeter was periodically irrigated using a micro-flow irrigation system, with drippers installed at each plant, during the cultivation cycle. Following the initial irrigation, which was carried out by applying a volume of water sufficient to return the entire volume of soil to the Field Water Capacity (FWC), a weekly irrigation rotation with an irrigation volume suitable for returning the soil moisture to the FWC was carried out (Allen et al., 1998). The crop water consumption between irrigations was calculated by weighing the individual lysimeter tanks with a trans pallet equipped with load cells. The difference in tank weight between the end of the previous irrigation and the start of the next one represents the water consumption during that time interval as well as the irrigation volume required to restore the soil's FWC. A probe was inserted in each experimental plot's lysimeter to test the validity of the irrigation scheduling criterion and maybe correct the specific volume of watering. A scanner outfitted with Diviner 2000 sensors from Sentek Technologies was used to monitor soil moisture. We were able to accurately monitor all components of the water balance and collect drainage water samples to trace any EC movement in the aquifer thanks to the lysimeters. In this regard, because the tomato test takes place in a protected setting, irrigation volume was purposely raised at a given moment during the growing cycle to induce drainage.

TABLE 1 Physicochemical Properties (Mw, Molecular Weight; Water Solubility; KOW, Octanol/Water Coefficient; pKa, Acid Ionization Constant) of the Selected ECs.

ECs	Molecular Weight g mol^{-1}	Chemical Structure	Chemical Class	Water Solubility mg L^{-1}	KOW	pKa
Clarithromicin	748		antibiotic	1.693 at 25°C	3.16	8.99
Trimethoprim	290.32		antibiotic	400 at 25°C	0.91	7.12
Sulfamethoxazole	253.28		antibiotic	610 at 37°C	0.89	1.6
Fluconazole	306.27		antifungal	4,363 at 25°C	0.25	2.27
Climbazole	292.76		antifungal	58 at 25°C	3.76	6.49
Diclofenac	296.1		anti-inflammatory	2.37 at 25°C	4.15	4.15
Ketoprofene	254.28		anti-inflammatory	51 at 22°C	3.12	4.45
Naproxen	230.26		anti-inflammatory	15.9 at 25°C	3.18	4.15
Metoprolol	267.36		beta blockers	0.4 at 25°C	1.88	9.7
Carbamazepine	236.27		antidepressants	18 at 25°C	2.45	13.9

Emerging contaminants extraction from waters, soils, and plant organs

The concentration of ECs in water samples (spiked wastewaters and leached waters) was evaluated using an online solid phase extraction (SPE) method using previously established analytical settings (UPLC-QTOF/MS/MS) (Montagna et al., 2020). To extract ECs from soils, the modified QuEChERS method (De Mastro et al., 2022b) was used. Before extracting ECs from various parts of the plant, roots were gently hand washed with tap water to remove soil residues, then rinsed with deionized water and blotted dry with a paper towel. Finely chopped roots, leaves, stems, and tomatoes were stored in a 50-mL centrifuge tube in the dark at -20°C until extraction. In a 50 mL plastic centrifuge tube, 2 g of roots, leaves, and stems or 10 g of tomato fruits were placed and spiked with the appropriate recovery surrogate. Except for the tomatoes, 6 mL of water was added to the centrifuge tubes before capping and vortexing for 1 minute. After thoroughly wetting the samples, 10 mL of Acetonitrile was added to the centrifuge tubes and shaken by hand for 5 minutes. After this step, only the leaves, stems, and fruits were allowed to rest for 15 minutes. After that, a salting out step with Citrate buffer (4 g $MgSO_4$, 1 g NaCl, 0.5 g NaCitrate dibasic sesquihydrate, 1 g NaCitrate tribasic dihydrate) was performed. For 5 minutes, the tubes were vigorously shaken by hand. Following that, the samples were centrifuged for 5 minutes at 3700 rpm, resulting in a phase separation of the aqueous and organic solvents. The upper ACN layer (6 mL) was transferred into 15 mL tubes for the clean-up step. Tubes containing 900 mg MgSO4 + 150 mg primary secondary amine (PSA) for roots, 900 mg $MgSO_4$ + 150 mg PSA + 150 mg octadecyl (C18) for leaves and stems, 900 mg MgSO 150 mg PSA + 15 mg graphitized carbon black (GCB) for fruits, were vortexed for 1 min. After centrifugation (5 min, 4000 rpm), the supernatant was filtered through a membrane filter (PVDF, 0.22 mm), and 1.5 mL was transferred into a screw cap vial for LC-MS/MS analysis to determine the concentration of ECs from the four replicates of each thesis.

TABLE 2 The volume of seasonal irrigation, total rainfall, drainage, and ECs intake during the tomato growing cycle.

Parameter	Unit	FW	TWWx1	TWWx3
Total rainfall during the tomato growing cycle (R)	mm	88	88	88
Seasonal irrigation volume (I.V.)	mm	620.8	620.8	620.8
Total amount of drained water (D)	mm	25.0	25.0	25.0
Irrigation on lysimeter (time of flowering)	L $lysimeter^{-1}$	250	250	250
Total ECs intake in lysimeters (time of flowering)	mg	0	50	150
Irrigation on lysimeter (end season)	L $lysimeter^{-1}$	449.7	449.7	449.7
Total ECs intake in lysimeters (end season)	mg	0	89.94	269.82

Statistical analysis

The ANOVA procedure was applied to all datasets using a randomized complete design with four replicates. A one-way ANOVA procedure (Christensen, 2020) was used with the irrigation typology (FW, TWWx1, and TWWx3) as fixed factors and the replication as random. The entire dataset was tested using the analysis of variance (ANOVA) assumptions. The normality distribution of the model's residuals was verified graphically (QQ- plot) and statistically (Shapiro-Wilk normality test). Furthermore, Levene's test was used to confirm homoscedasticity. The experimental design and random sampling for the different matrices met the final ANOVA assumption. When all three ANOVA assumptions were met, the ANOVA was applied to the model. Only when the ANOVA revealed a significant difference (p- value 0.05), was a post hoc analysis of the estimated marginal averages performed using Tukey's HSD (honestly significant difference) test from the R package agricolae (de Mendiburu and Yaseen, 2020).

Results

Water balance components

Table 2 depicts the main components of water balance (seasonal irrigation volume, rainfall, and drainage), as well as the total ECs intake in the lysimeters. The total amount of applied irrigation water (I.V.) was 620.8 mm, while the total amount of drained water (D) was 25 mm. The total rainfall for the tomato growth cycle (R) was 88 mm. Figure 4 depicts the total amount of water and ECs applied to the soil using the TWWx1 and TWWx3 irrigation treatments.

Concentration, accumulation, and fate of ECs

Figures 5 and 6 depict the final concentrations of ECs in soil and plant matrices (root, stem, leaf, and fruits) at the end of the cultivation cycle. The FW irrigation approach contained no significant concentrations of target ECs. The TWWx1 method acted differently for each matrix (Figure 5). Rather than the fruit, the leaves had high levels of two ECs, fluconazole, and carbamazepine. The residual pollutant amounts in plant tissues were not substantially different from zero. Fluconazole, carbamazepine, and metoprolol levels in plant leaves, roots, stems, and fruits increased significantly with the TWWx3 strategy (Figure 6). The concentrations of the remaining contaminants in plant tissues were not significantly different from zero. The largest quantities of the three pollutants observed in the plants (fluconazole, carbamazepine, and metoprolol) were found in the leaves in both irrigation treatments (TWWx1 and TWWx3), with lower but substantial concentrations reported in the stems, roots, and fruits.

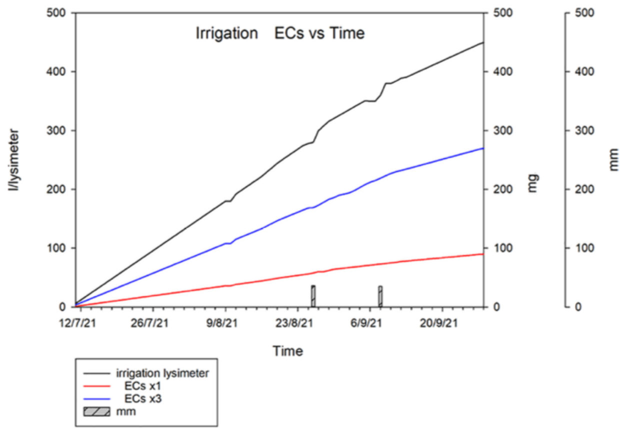


FIGURE 4
Cumulative water and ECs applied to the soil using fresh water (FW) and TWW effluent spiked with the addition of target contaminants in a dose comparable to the European average (TWWx1) and a triple dose (TWWx3).

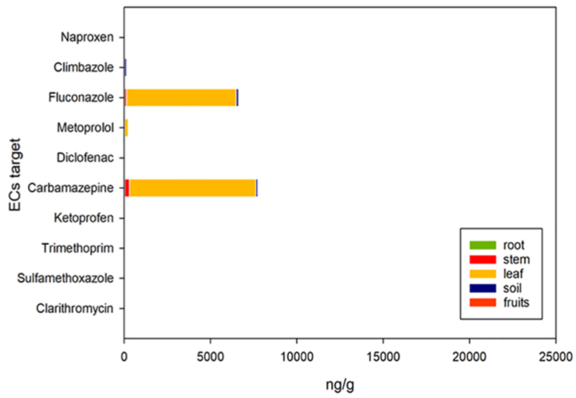


FIGURE 5
Cumulative concentrations of ECs in the plant-soil environment using fresh water (FW) and TWW effluent (TWWx1).

Martıń ez-Piernas et al., 2019 observed similar results, where organic microcontaminant concentrations were lower in tomato fruits, generally 10 times lower in fruit compared to leaves. Significant quantities of climbazole, fluconazole, carbamazepine, sulfamethoxazole, and clarithromycin were discovered in soil irrigated with TWWx1 and TWWx3 water. The other five pollutants in the soil had statistically negligible concentrations (Figures 5, 6). Results of Pico et al. (2019) study revealed the potential uptake and accumulation by crops of carbamazepine (as 10,11-carbazepine epoxide), atenlolol, caffeine, gemfibrozil and ibuprofen (as ibuprofen hexoside). Some pharmaceuticals and seven pesticides were detected in plants. Pharmaceuticals and ECs were found in quantifiable levels in all irrigation water, soils, and plants (>99.6%) in Israel (Ben Mordechay et al., 2022). Martıń ez-Piernas et al. (2019) revealed the presence of 17 OMCs in leaves and 8 in fruits with a higher frequency of detection of carbamazepine, evidencing their higher capability of uptake and translocation within the plant. Sunyer-Caldú et al. (2023) found that pharmaceuticals were the most frequently detected ECs in soils and waters, whereas UV filters achieved the highest concentrations. Diclofenac and salicylic acid were the most accumulated in soils, and diclofenac, ofloxacin, and benzophenone-4 were the most prevalent in the WWTP effluent. Camacho-Arévalo et al. (2021) analyzing the fate of sulfonamide antibiotics in tomato crops in commercial greenhouses in Almerıá (Spain) found that sulfamethoxazole was the antibiotic with the highest concentration in tomato fruit and irrigated soils. Christou et al. (2017) in a long-term (three consecutive years) wastewater irrigation of a tomato crop found that the highest soil concentration was due to sulfamethoxazole whereas diclofenac displayed the highest fruit concentration. The concentration of the studied pharmaceuticals in both the soil and tomato fruits varied depending on the qualitative characteristics of the treated effluent applied and the duration of WW irrigation. EC concentrations in irrigation water, as well as their physiochemical properties (primarily charge and lipophilicity), are the primary determinants of their translocation and accumulation in the soil-plant continuum (Ben Mordechay et al., 2022).

Mass balance of the ECs

The mass balance of the 10 ECs presented in this study was computed using the lysimetric technique utilized in this investigation for the soil, plant, and water compartments. Tables 3 and 4 indicate the total ECs intake in the systems (lysimeter) via irrigation water (90 and 270 mg/lysimeter of each EC, respectively, plus the amount present in the freshwater); the same tables also show the number of ECs detected in plants, leached water, and soil in the TWWx1 and TWWx3 treatments. The not detected column is the residue of the mass balance between ECs intake and the measured sum of ECs accumulated in plants, leached water, and soil. According to the mass balance, no ECs were found in the FW treatment; however, contaminants accumulation in the soil-plant- water system was measured for some ECs in the TWWx 1 (Table 3) and TWWx 3 (Table 4) treatments, with varying behaviour among the ECs. Naproxen and diclofenac were not found in the plant tissues, soil, or drainage water of any of the irrigation treatments (Tables 3, 4). This means that nearly all of these ECs are degraded in different chemical by-products. Ketoprofen behaved similarly to naproxen and diclofenac, except for a 1% accumulation in the soil in the TWWx3 treatment (Table 4). Climbazole, clarithromycin, trimethoprim, metoprolol, and sulfamethoxazole accumulated in the soil as a percentage of the total amount of irrigation added to the system, with values ranging from 100%, 47%, 13%, 11%, and 4% in TWWx1 to 91%, 75%, 16%, 31%, and 6% in TWWx3 (Table 3, 4). Except for climbazole (1% in TWWx3) and sulfamethoxazole (3% and 8% in TWWx1 and TWWx3) in drainage water, no accumulation of these five ECs was detected in plant tissues or leached water. We assume that naproxen and diclofenac were degraded in by-products because the residual amount of these five ECs concerning total intake was not detected.

Fluconazole and carbamazepine were found in the soil, plant tissues, and drainage water. Carbamazepine accumulated in plant tissues, drainage water, and soil at a rate of 3%, 1%, and 49% of the total amount added to the system with irrigation in TWWx1 and 4,5%, 4%, and 39% in TWWx3. The balance that was not detected (47% and 53% in TWWx1 and TWWx3) is assumed to be degraded in by-products (Tables 3, 4). Fluconazole accumulated in plant tissues, drainage water, and soil at rates of 2%, 14%, and 58% in TWWx1 and 2.5%, 17%, and 70% in TWWx3. The balance's undetected residual (26% in TWWx1 and 11% in TWWx3, respectively) is assumed to be degraded in by-products (Tables 3, 4).

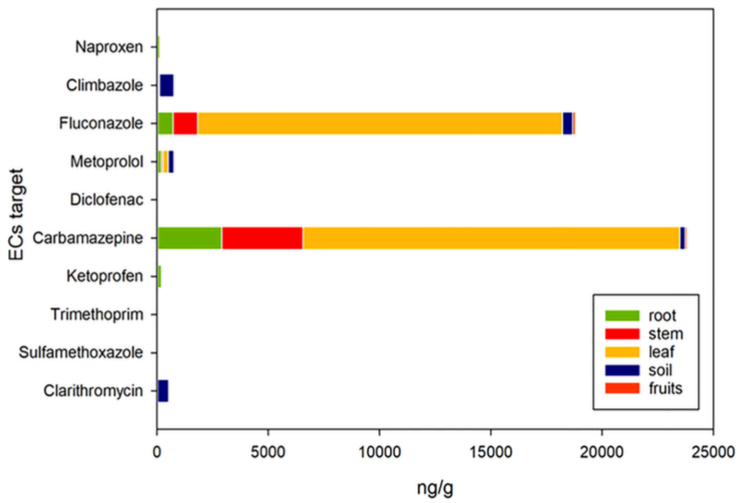


FIGURE 6
Cumulative concentrations of ECs in the plant-soil environment using fresh water (FW) and TWW effluent (TWWx3).

TABLE 3 Total intake and EC accumulation in plants, leached water, and soil lysimeters in the TWWx1 treatment (mean values of three replicates are shown).

Late season TWWx1 (mg lysimeter^{-1})					
Target	**Plant**	**Leached water**	**Soil**	**not detected**	**Total ECs intake**
Clarithromycin ***	0 c	0 c	41.99 b	47.95 a	90
			47%	53%	
Carbamazepine ***	2.41 b	0.83 b	44.13 a	42.63 a	90
	3%	1%	49%	47%	
Fluconazole***	2.00 d	12.90 c	51.87 a	23.17 b	90
	2%	14%	58%	26%	
Climbazole ***	0 b	0 b	90.00 a	0 b	90
			100%		
Sulfamethoxazole ***	0 c	2.86 b	3.18 b	83.90 a	90
		3%	4%	93%	
Trimethoprim ***	0 c	0 c	11.61 b	78.30 a	90
			13%	87%	
Ketoprofen ***	0 b	0 b	0 b	89.94 a	90
				100%	
Diclofenac ***	0 b	0 b	0 b	89.98 a	90
				100%	
Metoprolol ***	0.07 c	0 c	9.72 b	80.15 a	90
			11%	89%	
Naproxen ***	0 b	0 b	0 b	89.94 a	90
				100%	

Different letters and * indicate statistical differences among different theses ($p < 0.05$). $p < 0.05$ (*), $p < 0.05$ (**), $p < 0.001$ (***), ns (non-significant).
The column not detected is calculated as a residual of the mass balance of each experimental treatment. The percentage of each voice of the mass balance is calculated with respect to the total ECs intake.

TABLE 4 Total intake and EC accumulation in plants, leached water, and soil lysimeters in the TWWx1 treatment (mean values of three replicates are shown).

Late season TWWx3 (mg lysimeter^{-1})					
Target	**Plant**	**Leached water**	**Soil**	**not detected**	**Total ECs intake**
Clarithromycin ***	0 c	0 c	202.44 a	67.38 b	270
			75%	25%	
Carbamazepine ***	10.03 c	11.12 c	104.65 b	145.02 a	270
	4.50%	4%	39%	53%	
Fluconazole***	6.37 d	44.68 b	189.24 a	30.1 c	270
	2.50%	17%	70%	11%	
Climbazole ***	0.9 c	0 d	245.17 a	24.56 b	270
			91%	9%	
Sulfamethoxazole ***	0 c	21.53 b	15.38 b	232.87 a	270

		8%	6%	86%	
Trimethoprim ***	0 c	0 c	44.23 b	225.77 a	270
			16%	84%	
Ketoprofen ***	0 c	0 c	2.25 b	267.4a	270
			1%	99%	
Diclofenac ***	0.04 b	1.64 b	O b	268.14 a	270
		1%		99%	
Metoprolol ***	0.27 c	0 c	83.23 b	186.31 a	270
			31%	69%	
Naproxen ***	0.4 b	0 c	0 c	269.71 a	270
				100%	

Different letters and * indicate statistical differences among different theses ($p < 0.05$). $p < 0.05$ (*), $p < 0.05$ (**), $p < 0.001$ (***), ns (non-significant).
The column not detected is calculated as a residual of the mass balance of each experimental treatment. The percentage of each voice of the mass balance is calculated with respect to the total ECs intake.

TABLE 5 Tomato fruits ECe concentrations and ECe leachate total amount in the three irrigation treatments (mean values of three replicates are shown).

ECs target	Fruits			Leachate		
	TWWx1 (ng g^{-1})	TWWx3 (ng g^{-1})	FW (ng g^{-1})	TWWx1 (mg lysimeter $^{-1}$)	TWWx3 (mg lysimeter $^{-1}$)	FW (mg lysimeter $^{-1}$)
Fluconazole	–	110 a	–	11.9 a	44.6 a	–
Carbamazepine	–	89.2 b	–	2.9 b	21.2 b	–
Metoprolol	–	1.2 c	–	0.9 c	11 c	–
Clarithromycin	–	0.4 d	–	0 d	1.5 d	–
Climbazole	–	0.3 d	–	0 d	0 e	–
Sulfamethoxazole	–	0.3 d	–	0 d	0 e	–
Diclofenac	–	0 d	–	0 d	0 e	–
Ketoprofen	–	0 d	–	0 d	0 e	–
Naproxen	–	0 d	–	0 d	0 e	–
Trimethoprim	–	0 d	–	0 d	0 e	–
Signif. codes	ns	***	ns	**	***	ns

The concentration of EC on tomato fruit

Table 5 shows the average EC concentrations in tomato fruits. All fruits' concentrations are given in fresh weight, with a ripe tomato containing 95% water and 5% dry matter. The results showed that the contaminants under study had varying concentrations and behaviours. None of the ten contaminants evaluated were discovered in significant concentrations in FW or TWWx1-irrigated tomatoes (Table 4, Figure 5). Some contaminants responded differently after TWWx3 treatment (Table 4, Figure 6). During the TWWx3 strategy, only fluconazole, carbamazepine, metoprolol, clarithromycin, climbazole, and sulfamethoxazole were identified in fruits. The concentrations of the individual compounds varied significantly: fluconazole was 110 ng g^{-1}, carbamazepine was 89.2 ng g^{-1} and metoprolol was 1.22 ng g^{-1}. Clarithromycin, climbazole, and sulfamethoxazole were found at 0.03 ng g^{-1} concentrations, which was statistically comparable to 0. Christou et al. (2017) discovered that diclofenac, sulfamethoxazole, and trimethoprim concentrations in soil were 0.35, 0.98, and 0.62 mg kg^{-1}, respectively. For fruit, diclofenac, sulfamethoxazole, and, trimethoprim concentrations were 11.63, 5.26, and 3.4 mg kg^{-1}, respectively. The average carbamazepine content in tomato leaves was8.9ngg−1whileinfruitwas0.23ngg−1(Martıńez-Piernasetal., 2019). In tomato mature plants grown on fortified water-irrigated plots, the concentration of carbamazepine was found to be 0.19 ± 0.32 ng g^{-1} (Wu et al., 2014). Ben Mordechay et al. (2022) discovered that the average EC content in soils was 129.4 88.5 g ha^{-1}, whereas the concentration of carbamazepine on tomato leaves was 546.4 557.5 ng g^{-1}.

Discussion

The European summers of 2018, 2019, and 2020 caused widespread and severe droughts, setting a new standard in Europe (Rakovec et al., 2022). Given the increasing scarcity and pressure on freshwater resources for irrigation, the use of alternative water resources such as treated wastewater is becoming more popular. The use of treated wastewater as a potential source of

fresh water is expected to gain popularity not only in arid regions but also in temperate climates (Hochstrat et al., 2006). However, it should be noted that (unregulated) de facto (indirect) reuse has been common practice for decades (Beard et al., 2019). A new EU regulatory framework now intends to stimulate and regulate the direct reuse of treated domestic wastewater for irrigation purposes (EU). Because responsible reuse is critical (Dingemans et al., 2020) a risk management plan is part of the EU regulation 2020/74, which includes the effect of water reuse on farmers, soil, groundwater, and ecosystems. However, there is currently no direct data on the effects of reusing treated wastewater irrigation under real-world agricultural conditions on the fate of a diverse variety of ECs (Narain-Ford et al., 2022). To date, only a few studies have shown that crop plants irrigated with treated wastewater in the field or in simulated field settings absorb and accumulate emerging contaminants. Quantifying the ECs investigated in the plant-soil environment is critical because it will provide a better understanding of crop plants' ability to absorb and accumulate ECs. In this study, we used a controlled lysimeter experiment to determine the fate of ECs in the soil-water-plant system. According to the findings of the current study, the fate of ECs in the soil-plant water system varies depending on the contaminant. Except for a very minor concentration of ketoprofen in soil irrigated with a triple dose of ECs, the total amount of naproxen, diclofenac, and ketoprofen delivered in lysimeters with irrigation water was not discovered in plant tissues, soil, or drainage water. This implies that 100% of these two ECs are rapidly degraded into by-products with distinct chemical compositions. The formation of by-products that are not necessarily less toxic than the starting compounds is a critical point that needs to be investigated further. Despite extensive research on ECs, little is known about the incidence and destiny of their by-products or metabolites in the environment. At the end of the growing cycle, climbazole, clarithromycin, trimethoprim, metoprolol, and sulfamethoxazole were found in the soil, but no accumulation was found in plant tissues or leached water, with the exception of a small amount of climbazole in plant tissues (1% in TWWx3) and sulfamethoxazole in drainage water (3% and 8% in TWWx1). It should be emphasized that the TWWx3 treatment was used to boost EC concentrations and stress the soil-plant reaction. The presence of clarithromycin, trimethoprim, metoprolol, and sulfamethoxazole in soil but not in plant tissues indicates that either tomato plants have a limited ability to adsorb them or soil particles have a high ability to adsorb them. The ability of the soil to absorb the aforementioned ECs could also explain their lack of drainage water. As with naproxen and diclofenac, climbazole, clarithromycin, trimethoprim, metoprolol, and sulfamethoxazole are assumed to be degraded in by-products in the plant-water system. The time required for degradation may be related to the difference in the percentage of ECs detected versus those not detected in the soil. In TWWx1, for example, metoprolol accumulation was recorded at 11% in the soil and 89% was not identified, implying a faster degradation time than climbazole, which had 100% accumulation in the soil at the same sampling time (Table 3). Carbamazepine and fluconazole were found in plant tissues, soil, and drainage water, and they were the least degraded ECs found in by-products. These data show that these two ECs are more persistent in the soil-water system and have a longer degradation period than the other ECs studied. Among the azoles, fluconazole, due to its complex chemical structure, comprising two triazoles and two chlorine atoms, is considered a persistent compound, unlike climbazole and sulfamethoxazole (Pacholak et al., 2022). Other research studies (Christou et al., 2017; Martıń ez-Piernas et al., 2019; Camacho-Arévalo et al., 2021; Sunyer-Caldú et al., 2023) have demonstrated that other contaminants such as diclofenac and sulfamethoxazole remain a concern. Carbamazepine is one of the most frequently detected ECs in soils irrigated with reclaimed water (Beltrán et al., 2020), and these findings suggest that these contaminants have a high potential for soil and water pollution. The results indicate also an uptake of carbamazepine and fluconazole by plants, as also reported by (De Mastro et al., 2023). In particular, the highest concentrations of the last two contaminants were found in leaf tissues, and only when we forced the ECs concentration in the TWWx3 treatment were carbamazepine and fluconazole found in fruit tissues. Most studies that found the absence of most added compounds in tomato fruits can be explained by increased water flow for transpiration towards the leaves, resulting in a greater accumulation of ECs in the leaves than in the fruits, as demonstrated by (Martıń ez-Piernas et al., 2019). Second, ECs taken up by the plant can be converted into phase I metabolites (for example, hydroxylation) and phase II metabolites, for example, by conjugating the progenitor chemical or phase II metabolites with glucose, glucuronic acid, and malonic acid (Mlynek et al., 2021). Our findings are supported by the metabolization of progenitor components, such as the absence of substances within the fruit, which is consistent with Kovačič et al. (2023). The lack of all of the examined ECs when tomato fruits received irrigation with water containing the average European pollutants concentration appears to imply that the reuse of treated wastewater might be considered a reliable water supply (Kovačič et al., 2023). However, the presence of carbamazepine and fluconazole in plant tissues (roots, stems, and leaves in TWWx1, and fruits in

TWWx3) in our study suggests that these two contaminants may be taken up and accumulated in the edible part of the tomato, posing a risk to human health and the food chain. Fruit contamination is possible at high ECs concentrations in irrigation water for Metoprolol (1,2 ng g-1 F.W.) and, at very low concentrations, for clarithromycin and sulfamethoxazole. (Bigott et al., 2022) and (Gallego et al., 2021) discovered a trend of higher concentrations of carbamazepine and climbazole in crops irrigated with treated wastewater.

To date, about 90% of emerging contaminants are disposed unscientifically into water bodies, creating problems to public health and environment. Their mitigation remains mainly limited by economic factors. Analysis is also very time consuming and costly and requires access to highly sophisticated equipment. Tarpani and Azapagic (2018) found that the life cycle for advanced effluent treatment range from 0.112 £ m-3 for ozonation based to 0.238 £ m^{-3} the highest for solar-Fenton processes. They concluded that advanced wastewater and sludge treatment would increase the costs of conventional wastewater treatment by 1.5–2.1 times. Pryce et al. (2022) analyzing the cost-effectiveness of graphene-based materials (GBMs) for EC removal found that the life cycle cost was 1.73 ± 0.09 \$ m^{-3} for graphene-oxide foam adsorbent, 2.97 ± 0.15 \$ m^{-3} for porous graphene adsorbent and 2.12 ± 0.11 \$ m^{-3} for a hybrid filter. Studies on the economics of advanced wastewater for removing EC are generally limited. As a result, more research is required to understand the long-term consequences on soil quality, crop productivity, and food safety, as well as a cost-benefit analysis of EC removal.

Conclusions

The effects of treated wastewater on fruit production, specifically tomato production, were investigated in this study. The behaviour of various target ECs in the plant-soil complex was studied and found to vary. Fluconazole and carbamazepine, in particular, were shown to have high plant absorption concentrations, with accumulation evident in the leaves, roots, and berries of the TWWx3 treatment. This imply that these two contaminants may be taken up and accumulated in the edible part of the tomato, posing a risk to human health and the food chain. However, other ECs (such as sulfamethoxazole, trimethoprim, ketoprofen, diclofenac, metoprolol, and naproxen) showed substantial uncertainties in their fate, which was most likely owing to degradation in the soil and cultivation factors. The study's findings support the premise that constant and proper monitoring of the quality of water used for crop irrigation is necessary to minimize economic and food-quality losses. When properly monitored, reusing treated wastewater for irrigation can be a safe approach in agriculture, and can help policymakers develop future legislative frameworks for sustainable water management. Wastewater reuse adheres to the circular economy principles applied to water management because it can relieve pressure on surface and groundwater resources, provide a more consistent supply of water that is less dependent on climatic variations, and supplement existing water sources. More research on the environmental and health implications of ECs in agricultural systems is required, particularly the creation of metabolites and transformation products, to provide a conclusive answer on the safety of treated wastewater for irrigation.

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Chapter 5. Fate of Emerging Contaminants in Durum Wheat: Perspectives for Food Safety and Agricultural Sustainability

This is the official draft submitted to the Original Research, Front. Soil Sci. - Soil Pollution & Remediation.

Abstract:

This study investigates the fate of emerging contaminants (ECs), specifically pharmaceuticals, in durum wheat crops cultivated on soil irrigated with treated wastewater in Southern Italy. Conducted in lysimeters (already irrigated in previous cropping cycles with wastewater), the experiment assessed the presence and distribution of ECs in soil and plant tissues. Three different level of ECs were compared: irrigation with fresh water, treated wastewater at European average contaminant levels 200 ppb (TWWx1), and a triple dose of contaminants (TWWx3). The findings reveal significant differences in ECs accumulation within the durum wheat, highlighting potential food safety and environmental health concerns. Carbamazepine and fluconazole were among the ECs with notable accumulation patterns, raising questions about the risks of pharmaceuticals entering the food chain. The study underscores the complexity of ECs behavior in agricultural settings and emphasizes the need for comprehensive risk assessments and guidelines for using treated wastewater in irrigation. This research contributes to the dialogue on sustainable agriculture and the safety of utilizing treated wastewater for crop irrigation.

Introduction

In the current global landscape marked by ongoing social and environmental issues, agriculture serves as a crucial factor in safeguarding our food security. Rice, maize, and wheat are essential crops, accounting for roughly half of the global caloric intake (Naeem et al., 2023), highlighting the profound impact of agricultural practices on the delicate balance of our planet's ecosystems and supporting populations worldwide. However, fast global population increase, uncertain global climate conditions, and the COVID-19 pandemic have all had a substantial impact on food production, posing a significant threat to food security. Urbanization, rapid industrialization, and the widespread use of agrochemicals in contemporary agriculture have all introduced new pollutants and a wide range of synthetic chemicals into the agricultural ecosystem throughout time (Bayabil et al., 2022; Radwan et al., 2023). Contaminants accumulate in the soil, reducing its productive potential, microbial activity, and total crop output (Sairam et al., 2023).

Reuse of treated wastewater (TWW) in irrigation has become a widespread practice in the Mediterranean, Middle East, and Asia. However, the use of treated wastewater for irrigation is not without its challenges, including soil salinity and potential health risks from pathogens and heavy metals, alongside complex socio-economic considerations. Lately, there has been a growing awareness and concern regarding the presence of novel pollutants in soil and irrigation waters. The rise of environmental pollutants and Emerging Contaminants (ECs) has emerged as a worldwide issue due to their adverse impact on the interconnected health of the environment, humans, and animals, thereby compromising the so-called One Health (Coccia and Bontempi, 2023), ECs could exist naturally or be synthesized for a variety of medical, industrial, and other practical everyday applications (Pradhan et al., 2023) Pharmaceuticals and personal care products (PPCPs) are one of the major worrying classes of ECs (Samal et al., 2022)because of their intrinsic capacity to trigger diverse physiological effects in humans (Osuoha et al., 2023) PPCPs can be transferred from soils to food crops due to the use of treated wastewater for irrigation (Colon and Toor, 2016).

Furthermore, long-term usage of contaminated irrigation water impacts plant ecosystem health, aquatic ecosystems, soil microorganisms, normal plant growth and development processes, and the quantity and quality of agricultural produce (Naeem et al., 2023). Thus, the interplay between the evolving landscape of agricultural practices and the emergence of new contaminants poses significant challenges for sustainable and environmentally friendly food production.

Understanding the concentration, behavior, and cycling of contaminants, along with their degradation pathways, is crucial for the remediation of these substances originating from various sources (Pradhan et al., 2023). PhACs behavior in agricultural soils is a complex process and has become a global issue. Pharmaceuticals such as trimethoprim, ibuprofen, and sulfamethoxazole have been detected in winter wheat grain, summer maize grain, and the topsoil (Li et al., 2024), while 56 pharmaceuticals and personal care products have been found in tomatoes, lettuce, and carrot, along with soil (Sunyer-Caldú et al., 2023). Yet, more knowledge of the magnitude and conditions of their occurrence in crop production.

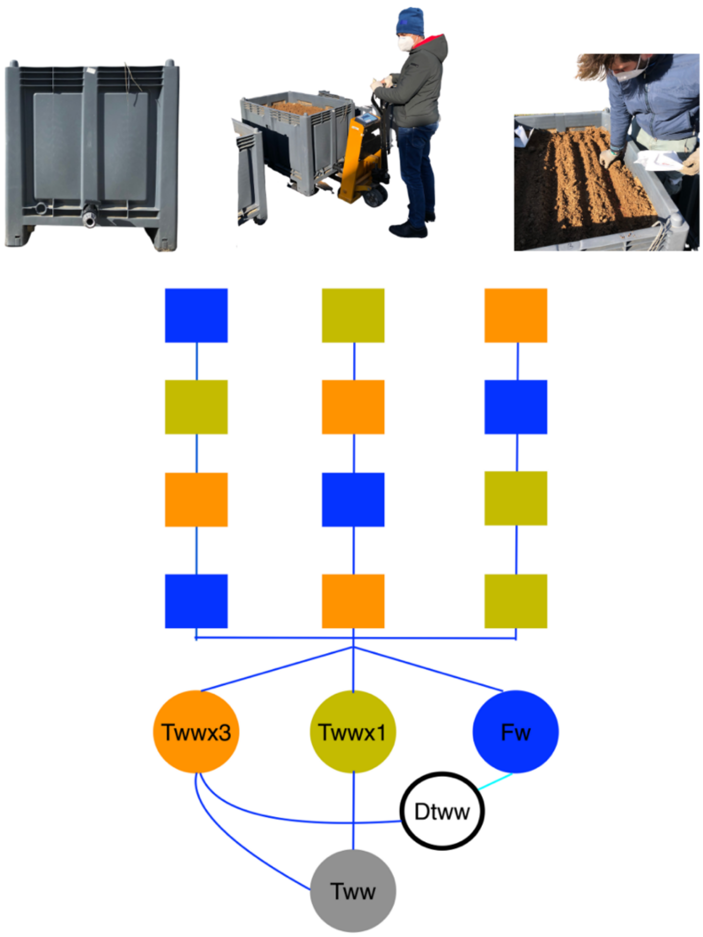
This research, building upon the work of Denora et al. (2023), investigates the destiny of emerging contaminants (ECs), particularly pharmaceuticals, in durum wheat crops cultivated on soil irrigated with treated wastewater in Southern Italy. The study makes a substantial contribution by offering novel and practical insights into the levels of emerging contaminants in cereal production irrigated with treated wastewater. This valuable data enhances our understanding of how these contaminants disperse in Mediterranean agricultural environments.

Materials and methods

The trial was carried out at the experimental site of the Centro Ricerche Agrobiologiche ALSIA Metapontum, located in the province of Matera, Italy, at coordinates 40.4029 N, 16.7944 E. The Mediterranean climate features hot, dry summers with average temperatures ranging from 24°C to 28°C, with moderate, wet winters and annual rainfall of 600-700 millimeters.

The "Saragolla" variety (*Triticum durum* Desf.) was sown on January 13, 2022, in the same pots previously utilized for growing tomatoes. The cultivation concluded with the harvest on October 12, 2022. Seeds were planted in lysimeters of 0.8 m^3 each, with 4 rows containing 90 seeds each and spaced 13 cm apart between rows for every experimental treatment. The distribution followed a randomized block experimental design (Figure 1) with four (4) repetitions.

Figure 1 *The experimental setup includes tanks for water treatments (TWWx1, TWWx3, Fw), lysimeters for various scenarios, and tanks for storing treated wastewater (TWW) and its safe disposal (DTWW).*



The experimental design involved the comparison of three irrigation treatments:

(I) irrigated with surface freshwater (FW) as control, obtained from the irrigation network system that is normally used by the farmers in the area for crop irrigation;

(II) irrigation with tertiary (TWW) municipal wastewater spiked with the addition of target contaminants in a dose comparable to the European average concentration (TWWx1);

(III) irrigation with tertiary (TWW) municipal wastewater spiked with emerging contaminants in a triple dose (TWWx3).

TWW was derived from the secondary sewage effluent of the municipal wastewater treatment plant (WWTP) in Ferrandina (Italy) using rapid sand filtration (rSF) followed by peracetic acid treatment (contact times greater than 60 minutes and doses of 2.5 mg/L). Table 1 shows the average values with standard deviation for the main conventional parameters of FW and TWW over the study period.

Table 1. *Main conventional parameters of FW and TWW were detected during the experimental period.*

Parameter	**Units**	**FW**	**TWW**
Total Suspended Solids (TSS)	mg/L	17.9 ± 15.1	23.4 ± 3.7
Biochemical Oxygen Demand at 5 days (BOD_5)	mgO_2/L	3.5 ± 0.7	39.8 ± 19.9
Total Nitrogen (TN)	mgN/L	3.3 ± 1.0	32.8 ± 21.5
Total Phosphorous (TP)	mgP/L	0.1 ± 0.0	5.9 ± 2.6
pH	-	7.9 ± 0.2	7.6 ± 0.1
Electrical Conductivity (EC)	mS/cm	0.9 ± 0.0	1.1 ± 0.1

TWW was used for both TWWx1 and TWWx3 irrigation treatments. Clarithromycin (CLR), sulfamethoxazole (SMX), trimethoprim (TMP), carbamazepine (CBZ), diclofenac (DCF), fluconazole (FLC), climbazole (CLB), ketoprofen (KTP), metoprolol (MTP), naproxene (NAP), triclosan (TCS), and gemfibrozil (GFB) were the Emerging Compounds (ECs) studied. These compounds were chosen specifically because they are commonly found in wastewater and are frequently not fully eliminated during typical wastewater treatment. Table 2 shows the concentration values of target ECs in TWW, which range from low ng/L to low µg/L (Ben Mordechay et al., 2021).

Table 2 *Concentration values of ECs detected in FW and TWW.*

ECs	Units	LOQ	FW	TWW
Clarithromycin	µg/L	0.01	<LOQ	0.4 ± 0.3
Sulfamethoxazole	µg/L	0.05	<LOQ	<LOQ
Trimethoprim	µg/L	0.01	<LOQ	<LOQ
Ketoprofen	µg/L	0.01	<LOQ	0.6 ± 0.6
Carbamazepine	µg/L	0.01	<LOQ	0.2 ± 0.1
Diclofenac	µg/L	0.01	<LOQ	3.7 ± 3.0
Metoprolol	µg/L	0.01	<LOQ	0.1 ± 0.1
Fluconazole	µg/L	0.01	<LOQ	0.1 ± 0.0
Climbazole	µg/L	0.01	<LOQ	0.1 ± 0.1
Naproxen	µg/L	0.10	<LOQ	<LOQ
Triclosan	µg/L	0.01	<LOQ	<LOQ
Gemfibrozil	µg/L	0.01	<LOQ	<LOQ

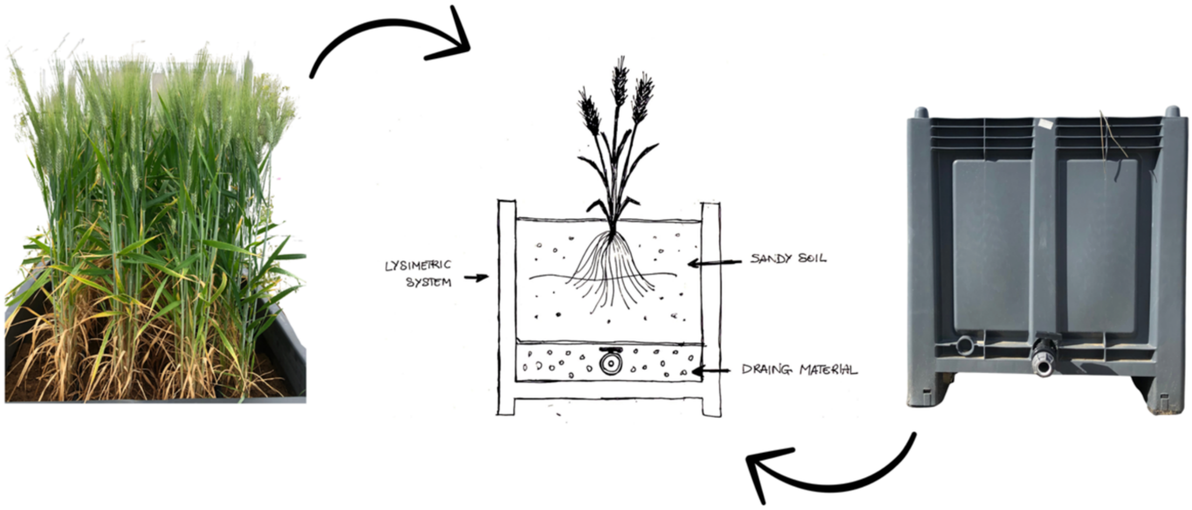
Table 3 summarizes the physicochemical parameters of the selected ECs. The multi-component standard solution (1000 ppm) was prepared using standards with a purity of more than 98%. This solution was added to irrigation wastewater at concentrations of 200 and 600 mg L^{-1} for each chemical, yielding TWWx1 and TWWx3, respectively. Before seeding durum wheat, the experimental soils were analyzed to determine the residual EC concentration from the previous season. These data indicate the beginning state (T0) and were critical for carrying out the mass balance assessment.

Table 3 *Physicochemical Properties (Mw, Molecular Weight; Water Solubility; Kow, Octanol/Water Coefficient; pKa, Acid Ionization Constant) of the Selected ECs.*

Compound	**Molecular weight (g/mol)**	**CAS number**	**Chemical Class**	**Solubility in water (mg/L)**	**Kow**	**pKa**
CBZ	236.27	298-46-4	antidepressants	18 at 25°C	2.45	13.9
CLR	748	81103-11-9	antibiotic	1.693 at 25°C	3.16	8.99
CLB	292.76	38083-17-9	antifungal	58 at 25°C	3.76	6.49
DFC	296.1	15307-86-5	anti-inflammatory	2.37 at 25°C	4.15	4.15
FLC	306.27	86386-73-4	antifungal	4,363 at 25°C	0.25	2.27
GFB	250.33	25812-30-0	antilipemic	11 at 25 °C	4.77	4.5
KTP	254.28	22071-15-4	anti-inflammatory	51 at 22°C	3.12	4.45
MTP	267.36	22204-53-1	beta blockers	0.4 at 25°C	1.88	9.7
NAP	230.26	22204-53-1	anti-inflammatory	15.9 at 25°C	3.18	4.15
SMX	253.28	723-46-6	antibiotic	610 at 37°C	0.89	1.6
TCS	289.5	3380-34-5	antibacterial	10 at 20 °C	4.76	7.9
TMP	290.32	738-70-5	antibiotic	400 at 25°C	0.91	7.12

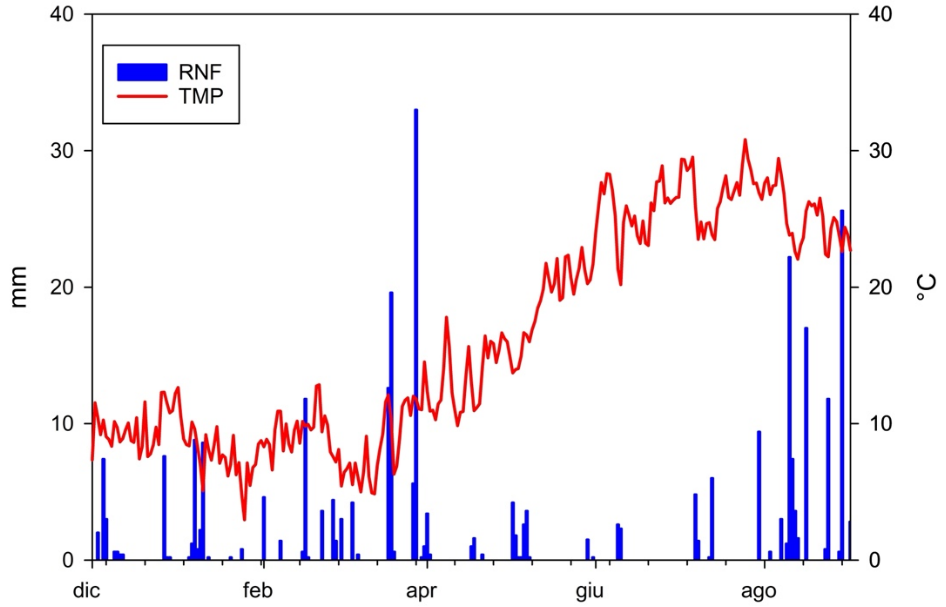
The experimental design included four lysimetric devices (plots) for each irrigation treatment. The same lysimeters used in the previous study (Denora et al., 2023) were employed to assess the effect of tomato's irrigation with wastewater on wheat (Figure 2). The soil under investigation is classified as sandy-loam according to the United States Department of Agriculture, with the following physical and chemical properties: sand 84.7%; silt 3.3%; clay 12.0%; field capacity (measured at 0.03 MPa) of 13.2% dry weight (dw); wilting point (measured at -1.5 MPa) of 7.2% dw; bulk density of 1.45 Mg m^{-3}; pH 8.3; electrical conductivity 0.10 dS m^{-1}; organic matter 0.32% (Walkley and Black method); available phosphorus (Olsen method) 35.6 mg/kg; total potassium 0.92 g/kg (determined using inductively coupled plasma optical emission spectrometry, Agilent, ICP-OES 720); total nitrogen 0.51% (Kjeldahl method); mineral NO_3-N 0.7 mg/kg; mineral NH_4-N 2.7 mg/kg.

Figure 2 *Schematic representation of the lysimetric weighing system, for determining water consumption, water flow, and mass balance of ECs.*



This soil type is characteristic of the Ionian-Metapontine coast and is extensively utilized for vegetable (Candido et al., 2013)and durum wheat cultivation. Additionally, the favorable hydraulic conductivity properties of this soil facilitated the monitoring of the circulating solution movement using moisture sensors. No irrigation interventions were planned, except at the end of flowering, where the aim was to assess the effect and uptake of ECs on the lysimetric system. This decision was also driven by adverse climatic conditions characterized by increased temperatures and the absence of precipitation in May and June (figure 3).

Figure 3 *Climograph depicting the period from December (Dec) 2021 to August (Aug) 2022, displaying precipitation (RNF) in millimeters (mm) as blue bars and temperature (TMP) in degrees Celsius (°C) as a red line. Precipitation is mainly concentrated between February (Feb) and April (Apr), with significant peaks exceeding 30 mm. Temperature shows a rising trend from December to June (Jun), reaching values close to 40°C.*



This allowed us to carry out irrigation interventions to restore the lysimetric system to field capacity. In the period from April to June 2022, a total of 200 liters per lysimeter were administered for the three compared treatments, with an added EC concentration of 40 mg L^{-1} for the TWWx1 treatment and 120 mg L^{-1} for the TWWx3 treatment. Each lysimeter underwent irrigation using a micro-flow system, with individually installed drippers, during the late flowering phenological stage of durum wheat. Following the initial irrigation, aimed at restoring the entire soil volume to its Field Water Capacity (FWC), a weekly irrigation rotation was implemented, providing an adequate irrigation volume to re-establish soil moisture at the FWC level (Allen, 1998). Crop water consumption between successive irrigations was quantified by weighing individual lysimeter tanks using a pallet jack equipped with load cells. The weight difference of the tank between the end of the preceding irrigation and the beginning of the subsequent one represented both water consumption during that period and the irrigation volume required to bring the soil's Field Water Capacity back to the desired level. A probe was inserted into each lysimeter in the experimental plot to verify the validity of the irrigation scheduling criteria and to make any necessary corrections to the specific irrigation volume. Soil moisture monitoring was conducted using a probe equipped with Diviner 2000 sensors from Sentek Technologies. All components of the water balance were meticulously monitored, and drainage water samples were collected to trace any movement of ECs in the aquifer through the lysimeters (figure 2). The choice to experiment lysimeters located in an open field rather than in a greenhouse, for a more precise simulation of real agricultural conditions, and considering that the durum wheat test occurred following the cultivation of tomatoes on the same lysimeters with the same experimental design, the irrigation volume was deliberately programmed for experimental purposes to optimally assess the absorption and fate of the selected ECs.

Extraction Procedure

For the ECs extraction from experimental soils, the modified QuEChERS method of De Mastro et al., (2022) was used. Since the QuEChERS extraction method was designed for samples with more than 75% moisture, for plant matrices such as straw and grain, was necessary to reduce the sample amount and increase the water added to make the sample pores more accessible to the extraction solvent (Díez et al., 2006; Pizzutti et al., 2007; Walorczyk, 2008). Before starting the extraction, the samples were pre-treated. To remove soil, roots were first washed with a light stream of tap water, rinsed with deionized water and then delicately dried with absorbent paper, while straw and grains were finely chopped using a mill. Samples were stored in a 50 mL centrifuge tube in the dark at –20 °C until extraction. 2 g of roots, 1 g of straw and 5 g of grains were placed in a 50 mL plastic centrifuge tube and 10 mL of water was added to all samples except for the roots which required 6 mL. After capping, tubes were vortexed for 1 minute. To the thoroughly wetted samples, 10 ml of ACN was added. The tubes containing straw, and grain were shaked by hand for 1 minute, while those containing roots were shaken for 5 minutes. In the specific case of straw, the sample was left to rest for 15 minutes. The method was followed by the salting phase with citrate buffer (4 g $MgSO_4$ + 1 g NaCl + 0.50 g NaCitrate Dibasic Sesquihydrate + 1 g NaCitrate Tribasic Dihydrate). The tubes were again shaken vigorously by hand for 5 minutes. Subsequently, for straw and roots, the samples were centrifuged for 5 min at 3700 rpm. Times were doubled for grain samples which were left to rest for two hours after this step. The phase separation between the aqueous and organic solvents obtained after centrifugation allowed to take 6 mL of the upper ACN layer using pipette. For the purification phase, the aliquot was transferred into 15 mL tubes containing 900 mg $MgSO_4$ + 150 mg primary secondary amine (PSA) for roots, or 900 mg $MgSO_4$ + 150 mg PSA + 150 mg octadecyl (C18) for straw and grain. After being vortexed for 1 minute, the tubes were placed in the centrifuge (5 minutes, 4000 rpm). The supernatant was filtered through a membrane filter (PVDF, 0.22 µm), and 1.5 mL was transferred to a screw-cap vial for LC-MS/MS analysis.

Statistical Analysis

For experimental continuity, the same statistical analysis procedure used in the previous year was followed (Denora et al., 2023).We employed the ANOVA methodology across all datasets within a randomized complete design featuring four replications. A one-way ANOVA procedure (Christensen, 2020) was utilized, incorporating the irrigation categories (FW, TWWx1, and TWWx3) as fixed factors and replication as a random variable. The entire dataset underwent scrutiny based on the assumptions of analysis of variance (ANOVA). The normal distribution of residuals from the model was assessed both visually (via QQ-plot) and statistically (using the Shapiro-Wilk normality test). Additionally, Levene's test was implemented to affirm homoscedasticity. The experimental design, coupled with random sampling for diverse matrices, fulfilled the ultimate ANOVA assumption. The ANOVA was applied to the model only when all three ANOVA assumptions were satisfied. Subsequently, a post hoc analysis of the estimated marginal averages was conducted exclusively in instances where the ANOVA revealed a statistically significant difference (p-value 0.05), employing Tukey's HSD (Honestly Significant Difference) test from the R package agricolae.

Results

Water balance components

At the beginning of wheat growing cycle, the soil moiusture was close to the field water capacity, due to the previous irrigation of tomato and to the rainy winter period. As a consequence, of the total 275 mm of precipitation (R), 204 mm of water drained during the beginning of cropping cycle (D). On the contrary the period between April and June, crucial for the vegetative activity of durum wheat, was characterized by a lack of precipitation and a rise in temperatures (Figure 3). In this last period 160 mm of irrigation water were applied to the lysimeters, providing a unique opportunity to study the introduction and interaction of ECs in the soil plant system.

We introduced two different cumulative concentrations of emerging contaminants, 40 mg/L and 120 mg/L, using treated wastewater (TWW) in the TWWx1 and TWWx3 treatments, respectively. These contributions added ECs to those already present in the soil system following the experiments conducted the previous year with tomato crops subjected to the same treatments.

Integrating the results of this experiment with those obtained from the previous analysis on tomatoes is essential to outline an overall picture of the mid-term behavior of emerging contaminants within the agricultural system. This continuity of research allows us to formulate more precise hypotheses regarding the mass balance of ECs and their environmental fate, providing fundamental insights for assessing the impact of irrigation practices with treated wastewater and for developing sustainable agricultural management strategies.

Emerging Contaminant Dynamics

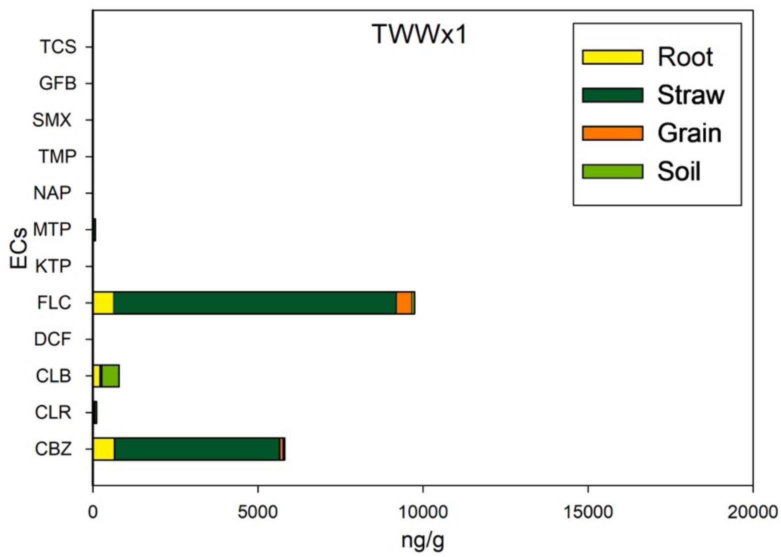
Figures 4 and 5, provide the concentrations of ECs in the soil and plant tissues (roots, straw, grain), measured at the end of cropping cycle respectively in TWWx1 and TWWx3 treatments. The application of FW for irrigation did not exhibit significant levels of ECs, presenting a stark contrast when compared to the use of spiked treated wastewater (TWWx1 - TWWx3). Notably, statistical tests confirmed that the differences in EC concentrations between the FW and TWW treatments were significant, with p-values well below the 0.05 threshold (table 4). The grain analysis between TWWx1 and TWWx3 treatments showed statistically significant differences in EC concentrations. For TWWx1, FLC was present at 464.26 ng/g and CBZ at 103.73 ng/g, while in the TWWx3 treatment, these concentrations increased to 979.51 ng/g and 526.89 ng/g, respectively, indicating a dose-response relationship. These results suggest that higher concentrations of ECs in irrigation water and soil are associated with increased accumulation in the grain, which could have significant implications for food safety and human health.

Table 4 *Statistical Analysis Results of EC s in soil and tissues (FW, TWWx1, TWWx3)*

ECs	soil and tissues FW	soil and tissues TWWx1	soil and tissues TWWx3
CBZ	ns	***	***
CLR	ns	**	**
CLB	ns	***	***
DFC	ns	ns	ns
FLC	ns	***	***
GFB	ns	ns	*
KTP	ns	ns	*
MTP	ns	***	***
NAP	ns	ns	ns
SMX	ns	ns	ns
TCS	ns	ns	*
TMP	ns	*	*

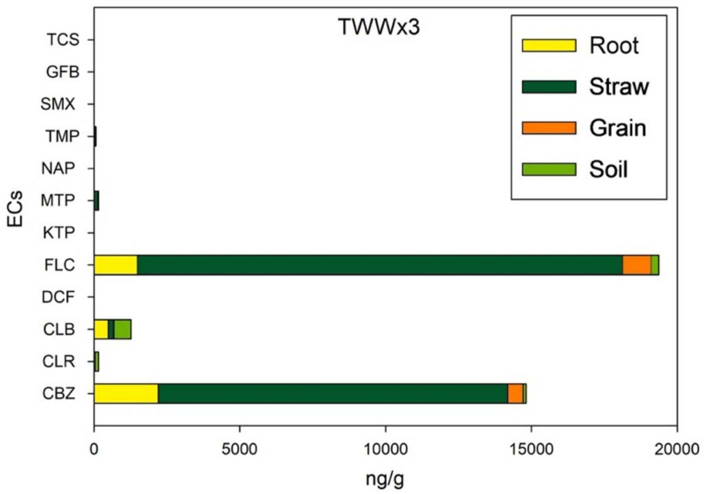
*Different * indicate statistical differences among different theses (p < 0.05). p < 0.05 (*), p < 0.05 (**), p < 0.001 (***), ns (non-significant).*

Figure 4 *Concentrations of ECs (ng/g) found in soil and tissues of durum wheat cultivation, related to the thesis (TWWx1).*



Further statistical comparisons of ECs across different plant parts indicated that CBZ accumulation in the straw was significantly higher than in the other portions of the analyzed system, with TWWx1 registering 4999.10 ng/g and TWWx3 at 11985.81 ng/g. These results align with the greater presence of CBZ in leaves rather than fruits as reported by Martínez-Piernas et al., (2019). Similarly, CLR levels in roots and soil were significantly different in TWWx1 and TWWx3 treatments, supporting the selective absorption dynamics discussed by Camacho-Arévalo et al., (2021). The concentrations of CLB in soil and plant parts also showed statistically significant differences, indicative of potential bioaccumulation. This is evidenced by the soil concentrations for TWWx1 and TWWx3 treatments being 524.73 ng/g and 596.39 ng/g, respectively. Conversely, the absence of DCF in all matrices across both treatments points to its potential degradation, which corroborates the findings of Christou et al., (2017).

Figure 5 *Concentrations of ECs(ng/g) found in soil and tissues of durum wheat cultivation, related to the thesis (TWWx3).*

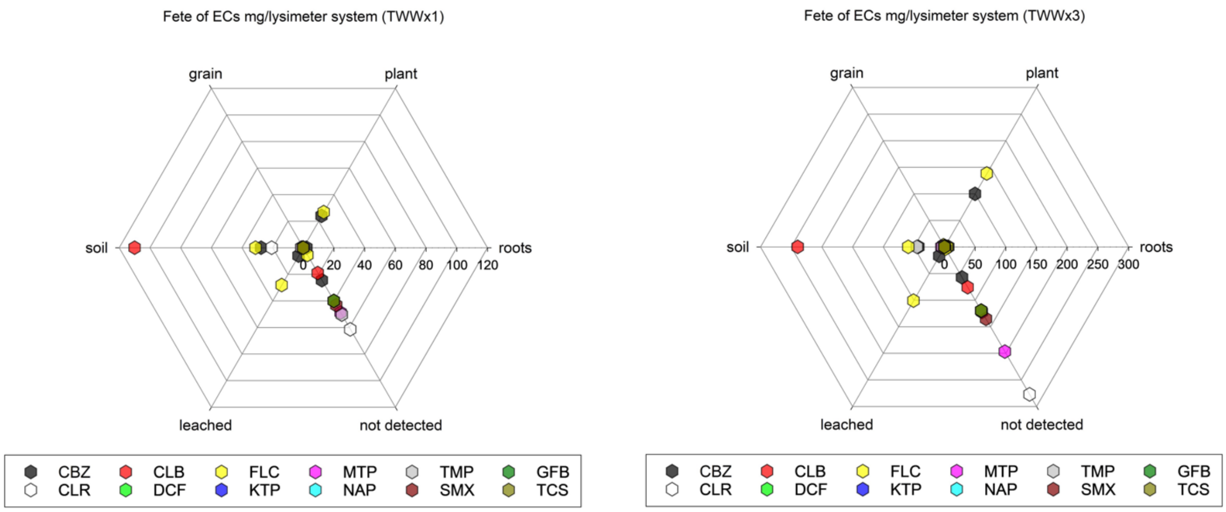


The presence of FLC in straw, roots, and grain in both TWW treatments further supports its significant absorption and translocation within the plant system, as suggested by the results of (Sochacki et al., 2021; Ben Mordechay et al., 2022; Pérez et al., 2022; Denora et al., 2023). The absence of KTP, NAP, and SMX in plant and soil samples indicates ineffective absorption or degradation. Variations in MTP presence between treatments were statistically analyzed, reflecting the significant influence of environmental conditions and agricultural practices on the ECs' behavior. The detection of TMP in roots and soil only in the TWWx3 treatment was statistically significant, which confirms its absorption as noted by Pico et al., (2019). Similarly, the low concentrations of GFB and TCS in roots and soil suggest limited absorption capacity or degradation propensity. This analysis highlights that the absorption and retention of ECs are significantly affected by the irrigation regime with treated wastewater. The marked differences are a result of the EC concentration in the irrigation water, the physicochemical properties of the contaminants, and the plants' intrinsic capacity for assimilation and translocation.

Mass Balance Analysis of Emerging Contaminants Using Lysimeter Technique in Agricultural Settings

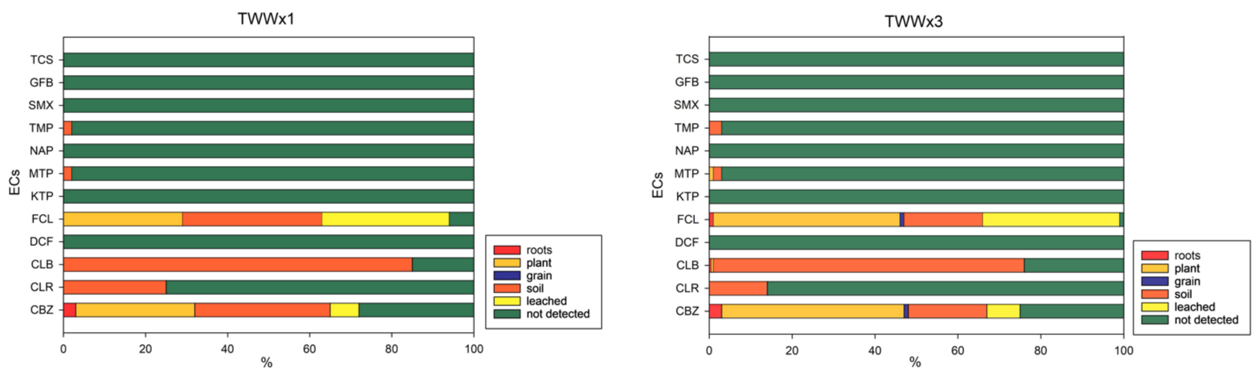
The utilization of the lysimetric technique in this study has proven to be pivotal in conducting a comprehensive assessment of 12 ECs as they traverse the soil, plant, and leachate compartments; The Mass balance of ECs using this technique provides a clear analysis of how these contaminants distribute, accumulate, and transform within the soil plant and water environments. The statistical analysis highlighted significant differences for each analyzed EC compared to the lysimetric system (Table 5). The analysis of the results highlight profound disparities in the behavior of these ECs, particularly when subjected to different concentrations of ECs in TWWx1; TWWx3 Figure 6-7.

Figure 6 *Mass balance analysis of ECs. On the left, it illustrates the fate of ECs when subjected to the treatment TWWx1, while on the right, it depicts the fate of ECs under the treatment TWWx3. The amount of ECs in soil leached water and plant is in mg/lysimeter.*



Taking CBZ as a case study, we observed substantial dispersion within the system under the influence of TWWx1, with elevated concentrations in roots (2.17 mg/lysimeter, constituting 3% of the total detected) and mainly in soil (27.48 mg/lysimeter, constituting 33% of the total). However, under the TWWx3 treatment, the majority of CBZ was found within the aerial components of the plants (99.83 mg/lysimeter, constituting 44%). This points to a pronounced absorption capacity by the plants, accompanied by a lower accumulation in the soil (19%) and a notable increase in CBZ leaching (17.10 mg/lysimeter, constituting 8%) (Figure 7). This pattern aligns with previous observations in plants, where CBZ has shown a tendency to exhibit higher bioconcentration in leaves than in roots (as reported by Carter et al., 2014; Pérez et al., 2022; Miller et al., 2016; Sochacki et al., 2021) corroborating our findings. However, it's worth noting that the concentrations of CBZ in leaves can vary significantly across different studies, which can be attributed to varying exposure conditions, such as concentration in the media, exposure duration, and specific plant species characteristics, among other factors.

Figure 7 *Fate of ECs expressed as percentage of their presence respect to the total detected (%) within the soil-water-plant system.*



Similarly, FLC displayed noteworthy presence in the roots and soil under the TWWx1 treatment, but with a higher proportion of leaching (28.10 mg/lysimeter, constituting 31%). This implies greater mobility in the soil compared to CBZ. Under the TWWx3 treatment, FCL exhibited an exceptionally elevated concentration in the aerial parts (138.08 mg/lysimeter, constituting 45%), along with a significant leaching percentage (101.06 mg/lysimeter, constituting 33%). These findings suggest a heightened potential for transport through both soil and water, aligning perfectly with the observations made by (Denora et al., 2023; Sochacki et al., 2021). In contrast, for other ECs such as DCF, NAP, and TCS, no presence was detected in any part of the system. This leads to the possibility of complete degradation or concentrations below the detection limit. The absence of detection in the leachate further indicates that these compounds were not significantly transported through the soil or water (figure 7). It becomes evident that a substantial percentage of the studied ECs remained undetected, raising pertinent questions about the potential formation of unidentified metabolites or their interaction and immobilization within the soil or plant matrices.

Table 5 *Statistical Analysis Results of EC s in Lysimeter Systems*

ECs	*lysimeter sistem FW*	*lysimeter sistem TWWx1*	*lysimeter sistem TWWx3*
CBZ	ns	***	***
CLR	ns	**	**
CLB	ns	***	***
DFC	ns	***	***
FLC	ns	***	***
GFB	ns	***	***
KTP	ns	***	***
MTP	ns	***	***
NAP	ns	***	***
SMX	ns	***	***
TCS	ns	***	***
TMP	ns	***	***

*The Different * indicate statistical differences among different theses ($p < 0.05$). $p < 0.05$ (*), $p < 0.05$ (**), $p < 0.001$ (***), ns (non-significant).*

The lysimeter system (table 5), represents all components of the balance: grain, roots, plants, soil, drainage, and the undetected portion, which has been calculated as the residual of the mass balance for each ECs. The percentage of each component of the mass balance is calculated relative to the total EC intake, considering the initial presence of ECs (T0).

Discussion

The findings of this study significantly augment our understanding of the environmental fate of ECs in agricultural systems, in the context irrigation using TWW. The variable accumulation of ECs like CBZ and FLC in plant tissues, as observed in our study, raises critical questions about the safety of food grown under these conditions. In particular, these pharmaceuticals showed concentrations higher than those of the other contaminants. This result can be possibly due to (i) the intrinsic characteristics of each contaminant that determined such behaviour (De Mastro et al. 2023), (ii) the different degradability of many compounds by the microbial community or by photodegradation/oxidation processes (ASCAR et al., 2017). In addition, CBZ and FLC were the ECs found in straw and grain. Usually, the uptake of different compounds by plants depends on their molecules forms and chemical properties (Kodešová et al., 2019). Compounds of intermediate lipophilicity ($0 < Kow < 3$) and with molecular weight less than 500 can be easily taken up by plant roots (Yan et al., 2016). In this regard, CBZ and FLC were within the optimal range to ensure their translocation in plants (Koba et al., 2017). In addition, CBZ is characterized by a non-ionic nature and a low molecular weight (Kumar and Gupta, 2016), and these characteristics allow this molecule to pass easily through the membranes of the root system and accumulate in leaves, as reported by many other studies (Montemurro et al. 2017). For neutral molecules, hydrophobicity is considered as the most important property for uptake dynamics by plants (Carter et al., 2014). Therefore, the hydrophilic nature of carbamazepine can determine its presence in pore water of soil solution and its easy uptake by plants. The low hydrophobicity of carbamazepine can be responsible also to its consistent translocation in the aerial part of plants (Carter et al. 2014). Other studies reported a higher concentration of carbamazepine in the aerial parts of plants than the roots (Knight et al., 2018) suggesting a passive uptake of this compound not restricted by root membranes. The greater presence in straw of FLC compared to other pharmaceuticals was also found by (García-Valcárcel et al., 2016): they found that fluconazole can easily cross the root membrane efficiently by diffusion. Probably, the lowest pKa (2.27) of FLC compared to all the considered ECs can favor its uptake and translocation in plants, according to (Herklotz et al., 2010), who reported the highest concentration of ECs with the lowest pKa in cabbage and Brassica rapa.

This variability underscores the complex interactions within the agroecosystem involving ECs, as similarly noted in studies (Jones et al., 2021; Pullagurala et al., 2018; Shi et al., 2022, Denora et al. 2023a, De Mastro et al. 2023)reporting diverse behaviors of ECs in different agricultural settings.

The pronounced accumulation of CBZ in straw and the substantial leaching of FLC challenge us to understand the mobility and stability of these contaminants, as also seen in the work of Pérez et al., 2022, which highlighted the varying mobility of different ECs in agricultural soils. The absence of certain compounds like DCF, NAP, and SMX from plant and soil matrices, suggesting either their complete degradation or non-uptake by plants, aligns with the findings of Ponce-Robles et al., (2022) and Rout et al., (2021) who also reported differential uptake of various ECs by crops.

The increasing reliance on TWW, especially given the freshwater scarcity exacerbated by severe droughts in Europe during 2018-2020 (Rakovec et al., 2022), makes it crucial to understand these dynamics. Hochstrat et al., 2006 and Beard et al., 2019 emphasize the growing popularity of TWW use in both arid and temperate climates, highlighting the need for effective management practices.

Furthermore, the detection of ECs like FLC and CBZ in edible parts of crops necessitates immediate attention, as it poses potential risks to consumer health. This concern is echoed by findings from Denora et al., (2023), who also detected ECs in edible crop parts. The re-evaluation of wastewater treatment processes, as suggested by (Verlicchi et al., 2023) becomes imperative in mitigating these risks. The significant leaching of certain contaminants suggests potential broader environmental impacts, extending beyond the immediate agricultural context. This aligns with the concerns raised by (Khan and Barros, 2023) regarding the environmental implications of using TWW in agriculture. The presence of contaminants in the environment could have far-reaching effects on ecosystems and human health, necessitating the development of comprehensive guidelines and policies for the safe use of TWW, as recommended by (Verlicchi et al., 2023). Our study contributes to a growing body of research that seeks to balance the benefits of TWW utilization in agriculture with the protection of ecosystems and human health. It highlights the need for an integrated approach that considers both the agronomic and social implications of TWW use, as also advocated byHashem and Qi, (2021); Shi et al., (2022).

Conclusion

The application of lysimeter techniques for mass balance analysis has confirmed accuracy in measuring the behavior of ECs, thereby deepening our understanding, and serving as a valuable benchmark for subsequent studies. The presence of ECs like FLC and CBZ in the edible parts of crops demands immediate scientific and regulatory attention due to the potential health risks to consumers. Considering that the concentrations of the ECs in the spiked TWW were higher than those of the original TWW, it is reasonable to exclude their entry into the food chain. The absence of certain compounds, including DCF, NAP, and SMX in both plant and soil samples, may indicate their complete degradation or non-uptake by the crops, aligning with research demonstrating selective EC uptake by different plant species. Additionally, the substantial leaching observed for some contaminants points to potential extensive environmental repercussions, further stressing the urgency for comprehensive guidelines and policies governing TWW usage in agriculture.

Our study is perfectly aligned with the recommendations made by Verlicchi et al., (2023) who advocate for a comprehensive strategy to safeguard environmental, animal, and human health. They call for a concise list of priority ECs amidst the increasing chemical diversity and recommend enhancing monitoring efforts, standardizing research methodologies, investigating EC persistence, bioaccumulation, toxicity, and fate in soil and crops, as well as developing predictive models. These recommendations aim to promote the sustainable and safe use of regenerated water in agriculture, with a keen focus on public health and environmental protection. Our research supports and extends these suggestions by demonstrating the effectiveness of lysimeter techniques in evaluating EC behavior, thereby contributing to the development of more informed and precise guidelines for the use of treated wastewater in agricultural settings.

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General Conclusions

Precision Agriculture

The precision agriculture theme of this work has made substantial contributions to the understanding and application of advanced methodologies to optimize resource use and improve crop yield and quality. Through the integration of geophysical mapping and traditional nitrogen balancing, we have demonstrated how precision agriculture can serve as an effective tool for achieving sustainable agriculture. The adoption of VRT has underscored the potential to reduce the environmental footprint of agriculture while simultaneously enhancing fertilizer use efficiency and reducing nitrate pollution risks. The use of electromagnetic induction sensors, combined with machine learning techniques, has enabled the creation of high-quality prescriptive maps, which represent a valuable tool for the practical application of precision agriculture. These approaches not only reduce operational costs but also promote more targeted and sustainable resource management in agriculture. Furthermore, the comparison between uniform and variable nitrogen fertilization has highlighted the environmental benefits of using VRT, indicating a promising path toward sustainable extensification and increased eco-efficiency in wheat production in Mediterranean contexts.

Reuse of Treated Wastewater in Agriculture

The second research theme examines the use of treated wastewater for agricultural irrigation, emphasizing the importance of closely monitoring water quality to prevent economic losses and risks to food quality. This study has highlighted how the safe reuse of treated wastewater can significantly contribute to sustainable water resource management, aligning with circular economy principles.

The analysis of the presence of emerging contaminants in the edible parts of crops underscores the need for a critical evaluation of wastewater treatment practices to minimize health risks. These findings highlight the urgency of developing comprehensive guidelines and policies for the use of treated wastewater in agriculture, emphasizing the need for further research on the environmental and health impacts of emerging contaminants in agricultural systems.

Final Considerations

This doctoral work has thus provided significant contributions in two crucial areas for the advancement of sustainable agriculture: precision agriculture and the sustainable reuse of treated wastewater. While precision agriculture offers innovative tools for optimizing resource use and improving crop performance, the conscientious reuse of treated wastewater opens new perspectives for sustainable water management in agriculture. Both research themes underscore the importance of interdisciplinary and technologically advanced approaches to address the challenges of modern agriculture, promoting environmental sustainability and food security.