

Article



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Abstract: Available phosphorus (AP) is a key macropollutant predictor of ecosystem services as well as a crucial indicator of soil productivity. Long-term applications of this macronutrient and its implications on sustainability in the face of peak phosphorus harvest have raised some concerns in recent years. This study aimed to characterise the edaphic AP in nearly 15,000 ha of the Mediterranean basin, an agricultural study area whose intensification is increasing with time. Four typical Mediterranean reference soil groups (RSG)-Calcisols, Luvisols, Fluvisols and Cambisols-were analysed and compared for their AP in two different agricultural settings-rain-fed and irrigation-from 2002 to 2012, where 1417 and 1451 topsoil samples were taken, respectively. AP increased from 2002 to 2012 in the irrigated Luvisols (p < = 0.05), Fluvisols (p < = 0.01) and Cambisols (p < = 0.05), while irrigated Calcisols maintained its concentrations (p > 0.05) over time. For rain-fed soils, the AP did not reveal significant differences in time for all RSG (p > 0.05). Additionally, irrigated Fluvisols and Cambisols presented 9% (p < = 0.01) and 68% (p < = 0.01) higher AP concentrations, respectively, than the corresponding rain-fed RSGs in 2012. We provide predictive maps for both 2002 and 2012. These results suggest that this area is departing from the sustainable goals of ecosystem services equilibrium; proper management practices that counteract the anthropogenic pressures in the area should be adopted.

Keywords: Mediterranean basin; available phosphorus; anthropic pressure; ecosystem services; degradation

## 1. Introduction

An increasing demand for resources in the finite planet Earth has promoted interest in the assessment and sustainable use of edaphic resources in agricultural settings. Anthropic pressures are largely contributing to ecosystem services' unsustainability, particularly in the Mediterranean basin [1,2], with increasing soil salinity, sodicity, alkalinity, loss of organic matter (SOM) content and accumulation of phytonutrients, especially ones that may cause disruption to ecosystem services. Nitrogen (N) and phosphorus (P), usually limiting factors in an agricultural setting, are such sustainability disruptors due to edaphic intensification, with increasing inputs of fertilisers, phytochemicals and irrigation water, in an overall setting of local climate changes (i.e., an increase in temperature and a decrease in precipitation) [3,4], which exposes the pragmatic importance of embracing sustainable agriculture approaches in the Mediterranean area [5–8]. It is curious, nonetheless, that the European statistics on the balance of N and P in agricultural soils point towards a decrease in nutrients in the soils and also in the consumption of inorganic P fertilisers in the European Mediterranean basin countries [9,10]. On the other hand, authors such as Butusov and Jernelöv [11] state that the demand for P is increasing due to population growth and increased incomes in developing countries, resulting in a higher nutrition value of the new



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diet. Monteiro and Torent [12] state that the edaphic availability of P is fundamentally controlled by the equilibrium established between the phosphate concentration in the soil solid phase and its concentration in the soil solution (SS) and that European soils are saturated for P sorption due precisely to these high P concentrations in the SS. These concentrations are caused by anthropic P inputs being far superior to their outputs over time creating a positive balance where P levels in the soil are higher than those required by the crops, and contributing to the elevated and continuous diffuse pollution caused by N and P runoff and drainage.

The study of Yin et al. [13] states that the over-application of P fertilisers is adversely impacting ecosystem services and its sustainability; Butusov and Jernelöv [11] further this environmental impact alert and state that as long as water-soluble fertilisers are used for food production, between 10% and 30% of the deployed P, in the medium term, will be removed from the productive soil layers by surface and groundwater runoffs. These authors also draw attention to the fact that agricultural runoff is the principal cause of eutrophication in inland and coastal waters and that none of the measures recommended by the European Union (EU) for environmental impact waste management practices can be recommended for implementation while these kinds of fertilisers are being used. In studies performed in the Mediterranean basin assessing phosphorus form fractions and the differences in dominant P fractions between soil types, it was found that it is the phosphorus forms that dictate the edaphic P release potential, that phosphate fertilisation increases the soil labile P fraction with, mostly, inorganic P and that it is its management, in combination with the soil's pH value, other ions in solution and other intrinsic soil properties that affect the relative distribution of adsorbed and precipitated P [14–16].

According to Carreira et al. [17], the main geochemical factor that controls the fixation of P in arid and semi-arid ecosystems is  $CaCO_3$ , the leaching sequence resulting from the weathering of the bedrock in these ecosystems being Ca > Mg >>> P > Fe > = Al > Ti. In the typical Mediterranean calcareous soils, the low concentration of hydrogen phosphate in the soil solution is related to the adsorption surfaces, since in high concentrations, it precipitates mainly as calcium phosphate [18,19] and Delgado and Torrent [14], in a study carried out on Spanish, Italian and German soils, conclude that the availability of P in calcareous soils is lower than that of non-calcareous soils, due to the fact that metallic phosphates (i.e., Fe, Al and Ca phosphate) present in acid soils are more soluble than Ca phosphates in calcareous soils. In a study in Spanish calcareous soils, Borrero et al. [20] conclude that P sorption is significantly correlated with active and clay-sized CaCO<sub>3</sub>, but not with the total CaCO<sub>3</sub>.

This paper aims to improve knowledge on how available P concentrations vary between intensified and traditional agricultural systems in a study performed in an irrigation perimeter in four typical soils of a Mediterranean basin semi-arid region in real agricultural conditions (i.e., a non-controlled agricultural setting).

## 2. Materials and Methods

### 2.1. Study Area

The study was conducted in a Mediterranean basin field between the townships of Elvas and Campo Maior, Portugal, bordering Spain. The area is underlain by a combination of basic and hyperalkaline rocks. The area has a semi-arid environment according to the Thornthwaite climate classification system (DB2db4), with less than 500 mm of yearly precipitation and a mean annual evapotranspiration of approximately 813.2 mm [21]. This area includes the Caia irrigation perimeter where dozens of crops are present but the ones occupying the largest areas are: *Olea europea* L., *Zea mays* L., *Lycopersicon esculentum* Mill. and *Allium sativum* L. with a preponderance of 35%, 20%, 15% and 15%, respectively. The study area has become more intensified since the start of this study, with crops such as intensive olive groves being substituted with super-intensive ones. Additionally, the use of irrigation water has been increasing since 2002, with an overall 55% average increase in water usage until 2017 (e.g., rice, olive groves, overall orchards, pasture and tomato have

multiplied their water usage by 2, 3, 5, 5 and 2, respectively, from 2002 to 2017), which may be related to local climate changes [22]. For a better understanding of the crops present in the study area, please refer to Kaletová et al. [23]. The large crop variability associated with the different RSG, irrigation endowments, agricultural rotations and transitions, fertilisations, phytopharmaceuticals, etc., practiced in the irrigation perimeter does not allow us to describe them, except in the general terms presented here. The irrigation uses water of good quality, classified by the FAO classification system as C1S1 [24].

## 2.2. Soil Data and Analysis

A total of 1428 and 1451 topsoil samples were collected in 2002 and 2012, respectively. There are six main reference soil groups in the 15,000 ha that comprises the study area (Figure 1) where we studied the Luvisols, Cambisols, Fluvisols and Calcisols according to the FAO's World Reference Base [25]. A brief description of the dominant properties of the topsoil of these reference soil groups (RSG) for 2012 is presented in Table 1. Please refer to Telo da Gama et al. [21] for the 2002 edaphic description.



Figure 1. Soils of the study area according to FAOs classification system [25].

		pН	SOM	EC	Sand	Silt	Clay	Ca	Mg	К	Na	CEC	BSP
	Depth (cm)	(Water)	(%)	(dS m <sup>-1</sup> )		(%)				(cmol <sub>(+</sub>	<sub>+)</sub> kg <sup>-1</sup> )		
Fluvisols		6.59	1.22	157.1	72	13	15	8.26	2.13	0.40	0.17	21.6	49.3
Luvisols	0.00	7.21	1.31	158.9	70	12	18	17.8	3.28	0.45	0.19	29.1	71.8
Calcisols	0-20	8.04	1.53	148.8	50	21	29	11.68	2.42	0.50	0.15	37.4	86.2
Cambisols		6.33	1.34	135.1	71	13	16	7.12	3.04	0.40	0.17	21.9	48.1

Table 1. Main edaphic properties of the study area soils for 2012.

pH: hydrogen potential; SOM: soil organic matter; EC: electrical conductivity; CEC: cation exchange capacity (1 M NH<sub>4</sub>OAc at pH 7.0); BSP: base saturation percentage.

#### 2.3. Statistical analysis

Soil samples were dried at room temperature, sieved through a 2 mm screen, and then analysed for their available phosphorus content, which was extracted with a buffered solution of ammonium lactate and acetic acid at pH 3.65–3.75 [26]. They were then analysed by molecular absorption spectrophotometry at 650 nm in a UNICAM UV/VIS UV2 spectrophotometer after colour development, by adding a mixture of ammonium molybdate and ascorbic acid.

Statistical analyses were performed using the software package SPSS (v.25) where tests of normality (by Shapiro–Wilk) [27,28], inspection of kurtosis, skewness and standard errors [29–31] and visual inspection of the histograms, normal Q–Q plots and box plots were performed in the 2002 and 2012 sample data in order to assess if they were normally distributed. Tests for homogeneity of variances (Levene's) [32,33] were also performed in this subset in order to assess its homoscedasticity/heteroscedasticity. In the 2002 and 2012 sample data, we performed Independent Sample T-Tests on all normally distributed with homogeneity of variances data, and we applied the Central Limit Theorem when we had more than 30 samples per subgroup on our non-normally distributed, but with homogeneity of variances, data [34]. Data that showed non-normal distribution and with no homogeneity of variances were directly analysed by Mean Rank (MR) through the Mann-Whitney U Test (U) or the Kruskal-Wallis H test (H). All null hypotheses were rejected when p < = 0.05. Geographic information system analysis was performed in ArcGIS v 10.5 software package and the predictive maps were created with an Ordinary Kriging interpolation, which was adjusted for a logarithmic factor equation and, when available, aided by ancillary variables [35–43]. Non-predictive maps were created with the software package QGIS 2.18.27 'Las Palmas' [44].

#### 3. Results

From the beginning of this study (2002) to 2012, generally, in the study area, there were no significant changes in the content of available P in the soil (Table 2; p > 0.05).

**Table 2.** Temporal evolution of the available P (mg kg<sup>-1</sup>) in the study area from 2002 to 2012.

Parameter	Year Mean		Ν	Test	р
P (mg kg <sup>-1</sup> )	2002	140	1308	T(2(1(2)), 4) = 4	0.242
	2012	161	1310	-1(2010): -4.036	

P: Available phosphorus in the soil; T: Student's t test for two independent samples; *p*: *p* value.

While, in 2002, both agricultural systems presented the same available P concentration (p > 0.05), the parameter showed significant differences (p < = 0.05) when rain-fed and irrigated agricultural systems were compared in 2012, with the average content of available P in the irrigation system registering 23.2% higher concentrations than the ones in the rain-fed system (Table 3).

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Parameter	Year	AS	Mean	Ν	Test	р
	2002	Rain-fed	143	631	LI. 216 260 E00	0.605
$P(ma ka^{-1})$	2002	Irrigation	139	677	- 0:216,360.300	0.685
I (ing kg )	2012	Rain-fed	141	526	LI: 1(2 224 E00	0.000
	2012	Irrigation	174	784	- 0:162,324.300	

**Table 3.** Available P (mg kg<sup>-1</sup>) in rain-fed and irrigated agricultural system in 2002 and 2012.

P: Available phosphorus in the soil; CS: Agricultural system; U: Mann–Whitney U test; p: p value.

A comparative analysis between the two agricultural systems, considering the four RSG (Table 4), shows that the content of available P was the same for both agricultural systems for all RSG in 2002 (p > 0.05), while, in 2012, it was significantly higher in the Fluvisols (9.19%; p <= 0.05) and Cambisols (68.3%; p <= 0.05) in the irrigated agricultural system than in the rain-fed. In Luvisols, the available P concentration for the irrigation agricultural system is at the acceptability threshold (Table 4, Figure 2a,b; p = 0.055).

**Table 4.** Available P (mg kg<sup>-1</sup>) in rain-fed and irrigated agricultural system in 2012 by reference soil group.

Parameter	Year	RSG	AS	Mean	Ν	Test	р
		T-1 · 1	Rain-fed	136	222		0 704
		Fluvisols	Irrigation	123	394	- 0:44,455.500	0.734
		T · 1	Rain-fed	144	194	T (252), 0.770	0.442
	2002	Luvisols	Irrigation	173	160	- 1 (352): -0.770	0.442
	2002	0.1 * 1	Rain-fed	171	143	T (22(), 0.177	0.000
		Calcisols	Irrigation	187	85	- 1 (226): -0.177	0.860
		G 11 1	Rain-fed	100	61	T (OF) 1 144	0.055
$\mathbf{P}$ (m $\approx 1/2^{-1}$ )		Cambisols	Irrigation	77	36	- 1 (95): -1.144	0.255
$\mathbf{r}$ (mg kg $\mathbf{r}$ ) =		T-1 · 1	Rain-fed	d 144 198		LL 22 242 000	0.000
		Fluvisols	Irrigation	157	430	- 0:33,343.000	0.000
		T · 1	Rain-fed	160	152	T (228), 1 028	0.055
	2012	Luvisols	Irrigation	208	188	- 1 (338): 1.928	0.055
	2012	0.1 * 1	Rain-fed	156	99	T (227), 1 149	0.050
		Calcisols	Irrigation	189	130	- 1 (227): 1.148	0.252
		Contrate	Rain-fed	87.6	64	LL (0 <b>2</b> 000	0.001
		Campisols	Irrigation	147	36	- 0:692.000	0.001

P: Available phosphorus in the soil; RSG: Reference soil group; CS: Agricultural system; U: Mann–Whitney U test; T: Student's t test for two independent samples; *p*: *p* value.



**Figure 2.** Error bar, by RSG, for available P (mg  $kg^{-1}$ ) in (**a**) 2002 and (**b**) 2012.

Regarding the temporal evolution of the available P in the soils, for each agricultural system (Table 5), we conclude that, in the rain-fed system, the nutrients' edaphic concentration remained constant from 2002 to 2012 (p > 0.05), while, in the irrigated soils, there was a significant 25.0% increase (p < = 0.01).

**Table 5.** Available P (mg kg<sup>-1</sup>) in rain-fed and irrigated agricultural system in 2012 by reference soil group.

	Parameter	Year	RSG	Rain-Fed				Irrigation			
	i urunicici	icui	KUG =	Mean	Ν	Test	р	Mean	Ν	Test	р
(a)	P (mg kg <sup>-1</sup> )	2002 2012	Overall	143 141	631 526	T (1.155): 0.903	0.367	139 174	677 784	T (1.459): -4.027	0.000
(b)		2002 2012 Fluvisols	Fluvisols	136 144	222 198	T (418): -0.427	0.670	123 157	394 430	T (418): -0.427	0.005
	Р	2002 2012	Luvisols	144 160	194 152	T (344): 0.793	0.428	173 208	160 188	T (346): -2.032	0.043
	$(mg kg^{-1})$	2002 2012	Calcisols	171 156	143 99	T (240): 0.751	0.454	187 189	85 130	T (213): -0.388	0.698
		2002 2012	Cambisols	100 87.6	61 64	T (123): 0.893	0.374	76.9 147	36 36	T (70): -2.042	0.045

P: Available phosphorus in the soil; RSG: Reference soil group; T: Student's t test for two independent samples; *p*: *p* value.

A more detailed analysis (Table 5) reveals that the accumulation of available P occurred for all RSG under irrigation except for Calcisols (p > 0.05), increasing its content by 27.7 (p <= 0.01), 20.7 (p <= 0.05) and 91.7% (p <= 0.05), in Fluvisols, Luvisols and Cambisols, respectively.

From the analysis of Table 6, we conclude that the surface area with an available P concentration above 100 mg kg<sup>-1</sup> increased by 29.9%. In 2002, the "above 100 mg kg<sup>-1</sup> range already represented 66.9% of the soils in the study area and, in 2012, it represented 86.9%. From 2002 to 2012, there was a 261% increase in the area, with available P levels higher than 200 mg kg<sup>-1</sup>. A comparison of Tables 4 and 6 reveals that only the average crops on rain-fed Cambisols could experience increases in their yields using P fertilisation.

**Table 6.** Fertility class classification according to the content of available P in the soil [45] and the corresponding crop response. Available P for 2002 and 2012 in the study area.

P(mg kg <sup>-1</sup> )	Fortility Class	Crop Rosponso	2002		2012		
	renning Class	Clop Response	Area (ha)	%	Area (ha)	%	
<25	Very low	<50%	4.70	0.000	1.50	0.000	
25-50	Low	[50-75%]	672	4.40	131	0.900	
50-100	Medium	[75–95%]	4337	28.6	1860	12.3	
100-200	High	[95–99]	8825	58.2	8396	55.4	
>200	Very high	>99%	1319	8.70	4770	31.5	

The analysis of Figure 3a,b clearly shows that the increase detected in the available P concentration also occupies most of the study area. It should also be noted that only the crops grown on 13.2% of the total study surface (i.e., with soils with less than 100 mg kg<sup>-1</sup> of available P) would respond to fertilisation with P for most crops.



**Figure 3.** Available P content (mg kg<sup>-1</sup>) in the study area for (**a**) 2002 and (**b**) 2012.

# 4. Discussion

Although no overall significant differences in available P were detected from 2002 to 2012 and while, in 2002, the available P concentration did not differ between the rainfed cultivation system and the irrigation system, we registered a significantly greater concentration in irrigated soils than in rain-fed soils in 2012. This revealed the increased use of this macronutrient since 2002 in irrigated agricultural systems (e.g., through phosphate fertilisation or organic P amendments), increasing the labile fraction of P in the soils, which is in accordance with the study of Monteiro and Torent [12]. This intensification from 2002 to 2012 is more obvious when we compare both cultivation systems by RSG in both sampled years. While, in 2002, the available P concentration was the same in both agricultural systems for a particular RSG, in 2012, the Fluvisols and Cambisols revealed greater phosphorus concentrations due to the fact that this element is a key macronutrient and, therefore, its excessive use is a common practice in the irrigated system since it is mainly is applied in fertilisation systems in the form of NPK. Because the Fluvisols are an RSG that is closer to the rivers and irrigation points that feed the irrigation system, they are the soils that have been under irrigation for the most time (i.e., some have been under irrigation since 1969) and where cash crops are being grown. As stated in Telo da Gama et al. (2019), the Cambisols of the study area recently underwent an intensification that made for a 68.3% increase in available P (and also an increase in available K of 37% in the same period). The fact that Calcisols present no significant differences in available P concentrations between both agricultural systems may be attributed to the tendency that phosphorus has to precipitate with the  $Ca^{2+}$  ion, an element highly available in these soils, diminishing its solubility over time as the phosphorus continues to react with the

available  $Ca^{2+}$  in the soil (i.e., initially forming monocalcium phosphate ( $Ca(H_2PO_4)_2$ ), later, dicalcium phosphate ( $CaHPO_4$ ) and, finally, tricalcium phosphate,  $Ca_3(PO_4)_2$ ), which is demonstrated in the study by Carreira et al. [17].

The fact that, over time, there was no statistical difference in rain-fed soils is probably due to the more sustainable mode of production of this agricultural system and its balance between the inputs and outputs of the nutrients, especially when compared with the irrigated system that demonstrates an excessive use of phosphorus as a fertiliser in this cropping system. Therefore, over time, all RSGs except for Calcisols revealed an increase in available P in the irrigated agricultural system. The fact that the available P levels remained constant in the RSG Calcisols agrees with the results of most of the authors consulted [13,14,17,20], these data serving to reinforce the aforementioned proposition. Once again, we notice a greater rise in parameters in the RSG Cambisols in relation to the other RSG, where the available P almost doubled from 2002 to 2012, revealing the recent intensification that is taking place in these soils in their conversion from rain-fed to irrigated fields [21].

As for the fertility classes according to the edaphic available P content (Egnér Riehm), this table considers an average crop (adapted from the official Portuguese fertilisation manual [45]) and that the available P is the limiting factor of the crop (e.g., an available P concentration of 44 mg kg<sup>-1</sup> falls in the Low fertility class, which means that the crop productivity response will fall between 50% and 75% of the crop genetic capacity). In the results section, we showed that only the average crops on rain-fed Cambisols could experience increases in their yields using P fertilisation because of their "Medium" classification, meaning that, ceteris paribus, the crop could eventually express merely 75% of its total genetic potential and thus, phosphorus applications make agricultural sense. The remaining RSGs, regardless of the cultivation system, are in a high or very high fertilisation class, where the content of available P in the soils would allow most of the crops to express a minimum of 95% of their genetic potential, indicating that the response of the average crop to phosphorus fertilisation would be minimal to non-existent. In these cases, if fertilisation is to be carried out, it should be with the goal of nutrient maintenance in the soil only; this is not the case in the study area as there was a 261% increase in available P levels above the very high class (i.e., above the 200 mg kg $^{-1}$  where the genetic response of most crops is at a minimum of 99%). This result is not surprising since this is a nutrient that is frequently incorporated into agricultural soils in the form of NPK fertilisers, causing the specific and spatial variation registered in its contents to be motivated by agricultural practice. This surplus of available P could enhance the leaching of this element, contributing, together with N, to water eutrophication [45].

## 5. Conclusions

This multi-year study's findings demonstrated that intensification through irrigation in this 15,000 ha Mediterranean basin field has a tendency towards the accumulation of available P in Fluvisols, Luvisols and Cambisols. The presence of available Ca<sup>2+</sup> may have contributed to the observed equilibrium in available P in rain-fed and irrigated agricultural systems in Calcisols, as these soils are naturally rich in calcium. In contrast, all non-intensified soils maintained their edaphic available P, pointing to the overall greater sustainability of this agricultural system. Not surprisingly, the soils nearer the rivers and irrigation points, which have been under irrigation for the most time, or the ones that were recently intensified (e.g., converted from a rain-fed to irrigated agricultural system), are the ones that present the greatest increases in available P, enhancing the leaching of this element and contributing to water eutrophication. These results are but one more account of the anthropological impact on ecosystem services that is jeopardising its sustainability and proper conservation and could contribute to better land use.

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preparation, J.T.d.G; writing—Review and editing, J.T.d.G, J.R.N., L.L. and A.L.P; visualization, J.T.d.G, J.R.N., L.L. and A.L.P; visualization, J.T.d.G, J.R.N., L.L. and A.L.P; project administration, J.R.N.; funding acquisition, J.R.N. and L.L. All authors have read and agreed to the published version of the manuscript.

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