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Current anthropogenic pressures on agro-ecological protected coastal wetlands

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HIGHLIGHTS

- Direct and Indirect pressures of urban origin are found in l'Albufera Natural Park.
- Soil sealing was 18.6% in the administrative area in 2011, and 5.2% in the Park.
- A large number of pharmaceuticals (13 out of 17) were detected in surface waters.
- Connectivity is produced between densely populated areas, SWTPs and irrigated land.

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ABSTRACT

Coastal wetlands are areas that suffer from great pressure. Much of it is due to the rapid development of the surrounding artificial landscapes, where socio-economic factors lead to alterations in the nearby environment, affecting the quality of natural and agricultural systems. This work analyses interconnections among landscapes under the hypothesis that urban-artificial impacts could be detected on soils and waters of an agro-ecological protected area, L'Albufera de Valencia Natural Park, located in the vicinity of the City of Valencia, Spain. The methodological framework developed addresses two types of anthropogenic pressure: (1) direct, due to artificialisation of soil covers that cause soil sealing, and (2) indirect, which are related to water flows coming from urban populations through sewage and irrigation systems and which, ultimately, will be identified by the presence of emerging pharmaceutical contaminants in waters of the protected area. For soil sealing, a methodology based on temporal comparison of two digital layers for the years 1991 and 2011, applying Geographical Information Systems and landscapes metrics, was applied. To determine presence of emerging contaminants, 21 water samples within the Natural Park were analysed applying liquid chromatography tandem mass spectrometry for the detection of 17 pharmaceutical compounds. Results showed that both processes are present in the Natural Park, with a clear geographical pattern. Soil sealing and presence of pharmaceuticals are more intensive in the northern part of the study area. This is related to population density (detection of pharmaceuticals) and land cover conversion from agricultural and natural surfaces to artificial ones (soil sealing).

1. Introduction

World population is becoming increasingly urban. It is expected that people living in cities will account for two-thirds of the world's total inhabitants by the year 2050 (United Nations, 2012), giving rise to environmental impacts on a global scale (Hassan et al., 2005). As urban population concentration is greater in coastal zones (McGranahan et al., 2007), impacts on estuaries and coastal lagoons (due to their accessibility) may be more acute, exacerbating the historical degradation that has been going on for centuries (Lotze et al., 2006). Despite their richness in biodiversity, Mediterranean coastal wetlands are examples of the fragility of these areas because they are exposed to human activities such as farming systems (Readman et al., 1993) and constant urban sprawl (Li et al., 2010).

Pressures exerted by urban systems on the surrounding natural areas should be understood as direct (e.g. conversion and artificialisation of existing land covers) and indirect (e.g. externalisation of urban pollutants to natural and semi-natural landscapes), of which the main processes are anthropogenic soil sealing (Prokop et al., 2011) and outsourcing of (emerging) contaminants (Richardson, 2012) not treated in Sewage Water Treatment Plants (SWTPs), respectively.

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Soil sealing is defined as the covering of soil due to urbanisation and infrastructure construction. Thus, soil is no longer able to perform the range of functions associated with it (European Environment Agency, 2002). It is considered one of the most threatening soil degradation processes worldwide, and especially affects the pre-littoral and littoral areas of the Mediterranean ecosystems, where intensive urban development took place between 1970 and 2010 (UNEP/MAP, 2012). According to Wilby and Perry (2006), there is a continuous trend towards intensification of city-dwelling populations; a process that is likely to continue in the near future, which in turn makes the need to obtain accurate data on soil sealing spatial structures at local level more relevant.

Indirect pressures of urbanisation may be described as the type of undesirable actions in other (nearby or distant) natural or semi natural landscape entities. Pharmaceutical compounds for human treatment have been detected in aquatic environments (Brausch et al., 2012). They are considered emerging contaminants (EC). Richardson (2008, 2010, 2012) shows recent lists of EC, and their identification on water analysis (Richardson, 2009; Richardson and Ternes, 2011).

Approaches to help understand the dynamics of urban/artificial areas in the surrounding open space systems should be analysed taking in consideration distinct types of threats. The aim of this work is the development of an integral methodology, based on environmental forensic criteria (Murphy and Morrison, 2007) and Geographical Information Systems (GIS) (Longley et al., 2005), to determine the way direct and indirect pressures are exerted on natural ecosystems. Therefore, two types of processes (or main drivers) were analysed: the increment of artificial surfaces (direct pressures) and the flow of pharmaceuticals in surfaces waters (indirect pressure). The methodology was applied in the Natural Park of L'Albufera de Valencia and surrounding municipalities to obtain background on (1) how artificial surfaces extend from existing built up areas and (2) how prescribed substances travel from urban and agricultural water systems to the protected area.

The working hypothesis considers that there are transfer mechanisms of urban processes to nearby protected natural landscapes, represented by the enlargement and externalisation of artificial soil covers and the continuity of water flows. Therefore, connectivity between different environmental compartments is established regardless their dominant land use and level of environmental protection.

Specific objectives were (1) to determine rates and trends of artificial surface expansion represented by soil sealing and fragmentation; (2) to identify water paths of pharmaceutical compounds of urban origin and the hydrological connectivity between different environments (urban and agriculture); and (3) to establish spatial differences according to incidence of artificial surface expansion for soil sealing degradation, and to presence and concentration of pharmaceutical compounds contaminants.

2. Material and methods

2.1. Study area

The study was applied to L'Albufera de Valencia Natural Park and surrounding municipalities, located in Spain (Fig. 1). The original wetland area was evolved in the large alluvial plain formed by the river Turia to the north and the Júcar to the south. The area presents a complex relationship between its intrinsic natural importance (endemic species, biodiversity and hydrological buffering) and human activities (traditional agriculture and hinterland industrial and settlement development).

The current Natural Park covers 274.4 km^2, including its marine area. Due to secular alterations within its limits, a large proportion of the land belongs to rice fields, which occupy the primitive marshland, with only a few hectares still in their natural state (Soria et al., 2002). In the continental margins of the Natural Park, intensive irrigated farming is also found. A shallow lagoon is located in the centre; it is almost circular in shape and covers an area of 23.7 km^2.

The hydrology combines human management system and natural contributions, with water coming from the historic irrigation system as the main source of water inflows to the Natural Park. There is a very dense structure of overland artificial channels for irrigation, 59.7 km in length with a density of 323 m/km^2, with waters mainly coming from the rivers Jucar and Turia, which finally drain into the lake or directly to the sea. These water contributions, particularly those from rice fields, make up almost 70% of the total waters circulating the Natural Park and draining into the lake (Soria and Vicente, 2002). They are crucial in the function of ecosystems and in the recharge and chemistry of underground waters. Three channels connect the lake with the sea, their outflow being regulated by floodgates that maintain water levels in the rice fields.

In a small proportion, water inflows also arrive from the lake's own hydrographical basin, with an area of 917.1 km^2 in both directions as groundwater sources within the limits of the Natural Park and from several ravines. The main ones are La Rambla de Poyo and La Rambla de Beniparrell; other gullies end in ditches in the orchards and rice fields that flow into the L'Albufera.

The Natural Park is surrounded by a densely populated hinterland, due to the influence of the City of Valencia and its metropolitan area. Major pressures come from the activities of a population of 1,500,000 inhabitants, of which, almost 1,000,000 live in the thirteen municipalities included within the limits of the Natural Park. Farming and intensive irrigation systems developed in and out of the limits of the Natural Park are important threats to the preservation of ecosystems and water quality.

2.2. Methodology

2.2.1. Direct pressures: spatial representation, quantification and analysis of artificial surfaces

Two detailed concrete and asphalt artificial covers for the years 1991 and 2011 were created using ARCGIS (v. 10.1) GIS vector structure. For the year 1991, an information layer was produced from a panchromatic aerial photograph of 1991(provided by the Valencia Cartographic Institute) which was converted through GIS processes into an orthophoto. The resulting product was a full extent scene that covers the administrative study area, with a final pixel definition of 1 m. This precision allows the identification of very small soil sealing entities, considering the true smallest cartographic unit as having around 8 m^2 and the minimum linear feature width of 3 m. A present day artificial surface layer was constructed using the 2011 year colour orthophoto of 0.5×0.5 metres pixel resolution (provided by the Spanish National Geographical Institute). Information extraction was performed by on screen digitising following techniques of aerial photograph interpretation for land cover-use delimitation (Taylor et al., 2000).

The resulting layers were further integrated into a GIS analytical structure together with a coverage containing municipal boundaries of the administrative study area and another one including the limits of the Natural Park. All digital maps were geographically positioned following national and regional mapping standards: Spatial reference system ETRS89 and Universal Transverse Mercator projection. Based on existing metrics (Cushman et al., 2008), landscape (spatial) structure was analysed to determine the extent and trends of anthropogenic soil sealing and the degree of fragmentation and patchiness with the specific landscape class of paved and built up surfaces for both the municipalities of the administrative area and the protected land of the Natural Park. Soil sealing and fragmentation values were extracted for each year as absolute and relative surfaces.

Map overlay techniques (Gao, 2008) between the artificial surfaces and administrative entities and Natural Park layers were performed to obtain synthetic soil sealing values for each municipality and the total protected land respectively. Cartographic Diachronic spatial analysis was undertaken at administrative level using temporary municipal soil sealing trends between 2011 and the reference date (1991) and,

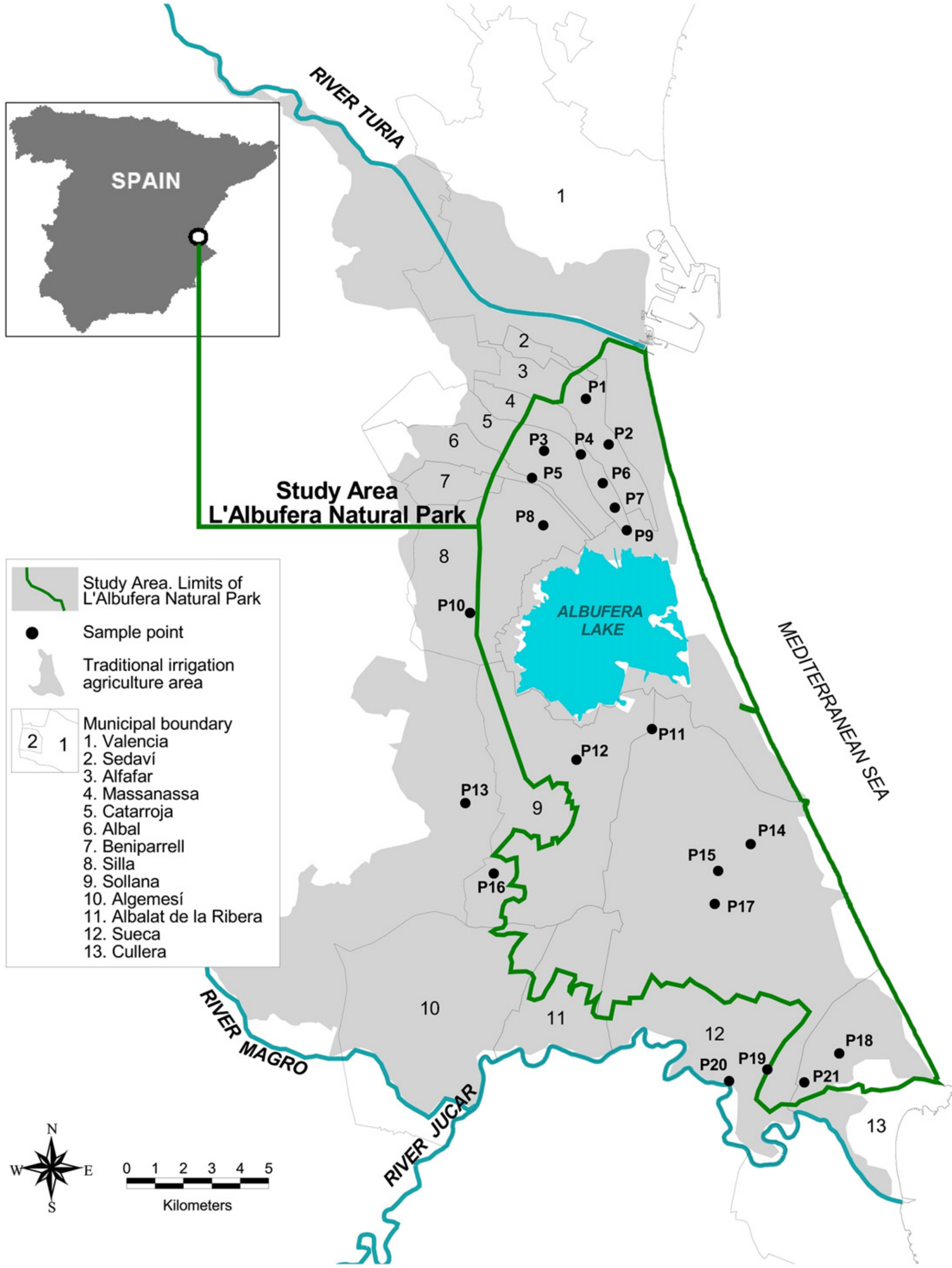

Fig. 1. Location of the study area and sampling points setting.

for the Natural Park, with the creation of a 500 m buffer density map (Griffiths and Dushenko, 2011; Xiang, 1993) which represented neighbouring and expansion effects of artificial surfaces towards the protected agro-environmental area.

Spatial fragmentation was analysed deriving synthetic metrics from both the total administrative surface (without considering municipal divisions to avoid non desirable added land fragmentation imposed by administrative boundaries) and the Natural Park land. Metrics obtained from each temporal layer were the total number of patches, the maximum patch size and, the average patch size (both in hectares), patchiness standard deviation and patchiness variance.

2.2.2. Indirect pressures: detection and spatial analysis of emerging pharmaceutical contaminants

Sampling was carried out in stable weather conditions, without any precipitation event for at least two weeks prior to the field campaign. Surface waters were collected at different points of the irrigation ditches in the traditional farming area to establish only spatial variations in their occurrence, without considering temporal dynamics. Sampling points were appropriately geo-referenced (UTM-ETRS89). A total of 21 water samples were taken, covering the most important channels (in the vicinity and inside of the Natural Park) that flow into the research area, following a monitoring pattern: points P1, P2, P3, P4, P6, P7, and

P9 were located in the irrigation zone and network whose waters are originally harvested in the river Turia, and they are also connected to the major municipal areas to the north of the Natural Park (Valencia, Sedaví, Alfafar, Massanassa, and Catarroja). The other sampling points were located downstream of several populations (Albal, Beniparrell, Silla, Algemesí, Sollana and Sueca), which also receive contributions from SWPTs and are connected to the irrigation system with waters harvested in the river Jucar.

Water samples were taken in clean polyethylene bottles (capacity 2.5 L) from the irrigation channels, typically in the middle of the channel at 30 cm depth. Before sampling, polyethylene bottles (2.5 L) were washed successively with detergent, tap water and distilled water. At the sampling point, the bottles were pre-rinsed with the sample water three times before taking the sample. The bottles were filled to the top with the water to remove air bubbles and maintained at 4 ºC until reaching the laboratory. Once there, samples were filtered through glass microfibre GF/A filters (Whatman, UK) prior to extraction, and stored in dark bottles at −20 °C until the analysis to avoid analytes degradation. The samples were extracted within 1 week,

Water samples were then analysed, in triplicate, for the simultaneous determination of 17 pharmaceuticals using Solid-Phase Extraction (SPE) and Liquid Chromatography Tandem Mass Spectrometry (LC–MS/MS), according to a previous methodology developed in our laboratory (Vazquez-Roig et al., 2011). The analytes were selected covering different therapeutic classes: β-blockers (metoprolol and propanolol), antidepressants (diazepam), anti-epileptic drugs (carbamazepine), analgesics (acetaminophen and codeine), non-steroid anti-inflammatory drugs (ibuprofen and diclofenac) and lipid regulators (clofibric acid and fenofibrate), in addition to seven antibacterials (ciprofloxacin, norfloxacin, ofloxacin, oxytetracycline, sulfamethoxazole, tetracycline and trimethoprim). The selection was made after a study of the consumption habits of the population of the area and the Valencia city.

The studied compounds were determined using Alliance 2695 HPLC module (Waters, Milford, MA, USA), and a Micromass Quattro LC triple quadrupole mass spectrometer (Manchester, UK), working in both positive and negative ionisation modes. Instrument control, data acquisition and evaluation were performed with Masslynx NT software (v. 3.4).

Spatial distribution of all information gathered was carried out using GIS techniques with ARCGIS (V. 10.1). Information obtained by different means (socioeconomic census, fieldwork, new GIS layers) was integrated into a common framework which would be used to explain the spatial representativeness of anthropogenic pressures on incoming surface waters of this Natural Park due to pharmaceutical products of urban origin.

Initial information consisted of (1) tabular data with municipal statistical values on the number of inhabitants for the year 2011 provided by the Spanish Institute of Statistics; (2) a digitised map with municipal boundaries; (3) Tabular descriptive information for SWTPs; (4) the digital reconstruction of the traditional irrigation systems (drainage networks) from existing published documents (Hermosilla Pla, 2006, 2007); and (5) data from the analysis of the water samples.

Population and derived population density records were incorporated as part of the associated database of the municipal boundaries layer. Tabular information describing SWTPs was geo-referenced as a point theme. Irrigation systems were generalised into a polygon theme of irrigated areas according to the water sources and another line layer with major irrigation channel distribution influent to the park. Water analysis results were incorporated as a point layer in the GIS structure.

Finally, to identify the presence of contaminants, both GIS layers and results from the pharmaceutical compounds determination were compared in the GIS environment and their spatial structure related to socio-environmental components.

3. Results

3.1. Trends in soil sealing and landscape fragmentation

Up to 46.7% of the municipal territory is within the protected land (Table 1). With varied proportions, most of them (eight) contribute with more than 40% of their administrative surface to the total 20,850 ha assigned to the Natural Park. The six largest municipalities account for 87.5% of the total administrative region and for 88.4% of l'Albufera Natural Park; Sueca, Valencia and Sollana are the municipalities with major contribution to the land inside the protected boundary (7251.4, 5734.2 and 2619.9 ha, respectively).

In 1991 a considerable part (14.9% of the total municipal extension) of the soils was already sealed by impervious and artificial surfaces. Intensities were variable among the thirteen studied municipalities. Most municipalities (Valencia, Alfafar, Massanasa, Catarroja, Albal, Beniparrell and Silla) had density values between 10% and 40%, while five had soil sealing intensities between 4.5% and 9.1% (Sollana, Algemesí, Albalat de la Ribera, Sueca and Cullera). With the exception of Valencia (which is the socio economic centre of the urban area with the highest population), low soil sealing densities were found in the two other major municipalities. Both Sueca and Sollana contribute in greater proportion to the agro-environmental Natural Park, with intensities of 6.5% and 4.5%, respectively.

In 2011, impervious surfaces had larger proportions in all municipalities with a general increment of 3.7% (1673.4 ha) of the total administrative extension (44,624.6 ha). Although individual municipal trends were very similar to the situation seen in 1991, some changes may be outlined. The maximum sealed surface extended up to 55.5% in one municipality (Sedaví); eight had density rates higher than 10%, and almost all of them had more than 20% of their area converted to artificial surfaces. Only four remained with values lower than 10% (Sollana, Albalat, Sueca and Cullera). The increments during the 20 year period oscillated from 1% (Albalat) to 7% (Valencia). Compared to the general administrative zone, the rates in the Natural Park are lower, although a similar trend was observed. In 1991 the sealed surface was 3.8% of the study area, with considerable differences when analysing the values obtained for the municipal land included in the Natural Park: artificial surface densities ranged from 2.3% to 20.7%, with most values below 6%. In 2011, sealed soils covered 5.2% (302 ha) of the total protected area, with a 1.4% added loss of land. All municipalities had more than 3% of their territory inside of the protected Park already covered by buildings, streets and roads.

Soil fragmentation has increased in both the municipal extent and the protected land (Table 2). In 1991 there were a total number of patches of 1507 and 331, respectively, while in 2011 the number rose to 2256 in the administrative zone (45.7% more) and to 558 in the Natural Park (increment of 68.6%). The increment of patches that occurred in the study zones may be the result of a compacting process of urban areas adjacent to existing ones and in the enlargement of roads and tracks, mainly done in open agricultural spaces found in the Park. This is also reflected in the rest of the metrics, with a reduction of the Mean and Maximum Patch Size. The conclusion is a trend to patch sizes homogenisation as suggested by the patch variance and the standard deviation.

Geographical concentrations of soil sealing processes are well identified. Rates of growth in both dates are higher in Northern municipalities (Fig. 2), with diachronic percentages of growth above 3%.

The consequence of this peri-urban trend is the continuity of the land-take process inside the limits of the Natural Park. Fig. 3 shows a map of 500 m parallel buffers with percentages of soil sealing increases in each of them. Neighbourhood effect occurs in the contact between the protected land and other municipal landscape units, where rates of increment are between 1% and 5%.

Table 1
Soil sealing trends (1991–2011) in both the administrative and agro-environmental Natural Park.

Municipality	Municipal surfaces			Soil sealing trends at municipal level						Soil sealing trends in the Natural Park					
	Total	In Study Area		1991		2011		Δ 2011–1991		1991		2011		Δ 2011–1991	
	(ha)	(ha)	(%)	(ha)	(%)	(ha)	(%)	(ha)	(%)	(ha)	(%)	(ha)	(%)	(ha)	(%)
1. Valencia	13,794.8	5734.2	41.6	3790.1	27.5	4754.6	34.5	964.5	7.0	180.1	3.1	323.3	5.6	143.2	2.5
2. Sedaví	177.6	19.7	11.1	88.4	49.7	99.0	55.7	10.6	6.0	1.0	5.3	1.1	5.6	0.1	0.5
3. Alfafar	1001.1	649.6	64.9	144.9	14.5	198.1	19.8	53.2	5.3	30.0	4.6	45.9	7.1	15.9	2.4
4. Massanassa	569.5	382.2	67.1	121.1	21.3	138.2	24.3	17.1	3.0	19.5	5.1	26.2	6.9	6.7	1.8
5. Catarroja	1280.6	630.5	49.2	228.3	17.8	284.7	22.2	56.4	4.4	29.5	4.7	37.9	6	8.4	1.3
6. Albal	726.4	93.4	12.9	167.8	23.1	197.9	27.2	30.1	4.1	7.7	8.1	10.0	10.7	2.3	2.5
7. Beniparrell	383.3	26.5	6.9	138.2	36.1	159.8	41.7	21.6	5.6	5.5	20.7	8.4	31.7	2.9	10.9
8. Silla	2509.7	1267.6	50.5	377.1	15.0	492.9	19.6	115.8	4.6	49.3	3.9	65.0	5.1	15.7	1.2
9. Sollana	3838.6	2616.9	68.2	174.3	4.5	263.9	6.9	89.6	2.3	60.0	2.3	81.1	3.1	21.1	0.8
10. Algemesí	4134.2	204.5	4.95	376.1	9.1	427.1	10.3	51.0	1.2	5.8	2.9	6.3	3.1	0.5	0.2
11. Albalat de la Ribera	1446.3	616.0	42.6	81.9	5.7	96.3	6.7	14.4	1.0	16.3	2.7	18.9	3.1	2.6	0.4
12. Sueca	9335.7	7251.4	77.7	609.6	6.5	744.3	8.0	134.7	1.4	326.7	4.5	395.2	5.4	68.5	0.9
13. Cullera	5426.8	1357.4	25.0	350.4	6.5	464.8	8.6	114.5	2.1	50.6	3.7	64.9	4.8	14.3	1.1
Totals	44,624.6	20,850.0	46.7	6648.2	14.9	8321.6	18.6	1673.4	3.7	782.1	3.8	1084.1	5.2	302	1.4

3.2. Emerging contaminants, presence and spatial distribution

Among the 17 pharmaceuticals screened in surface waters from the L'Albufera Natural Park, 13 (acetaminophen, carbamazepine, ciprofloxacin, codeine, diazepam, diclofenac, metoprolol, ofloxacin, propanolol, sulfamethoxazole, ibuprofen, clofibric acid and trimethoprim) were detected (Table 3); one of them (ciprofloxacin) was identified in very small concentrations, below the limits of detection (LOD). Tetracycline, oxytetracycline, norfloxacin and fenofibrate were not present in water samples.

16 (76%) water samples analysed were contaminated by pharmaceuticals. In these, carbamazepine was the substance most frequently detected (15 samples) with concentrations ranging up to 31.0 ng/L. The mean concentration (which was calculated by considering the non detected values as zero and those of samples less than the Method Quantification Limit (MQL) as the MQL) was 7.3 ng/L. Acetaminophen and ibuprofen were detected with frequency close to 50%, but at much higher mean concentrations of 860.3 ng/L and 207.7 ng/L, respectively. Sulfamethoxazole was detected in 43% of the samples at lower mean concentration than the previous one of 19.5 ng/L. Of the other pharmaceuticals, diclofenac and ofloxacin were found in 6 samples (29%), codeine, and propanolol in 5 (24%), ciprofloxacin, diazepam and clofibric acid in 4 (19%), trimethoprim in 3 (14%) and metoprolol in 2 (9.5%) with lower mean concentrations.

Five irrigation sectors are found within the limits of the Natural Park (Fig. 4). Each of them had different water harvesting sources. From north to south, two sectors collect waters and build their irrigation structures from the river Turia, where two water dams are constructed (both are found inside municipalities with population densities between 1000 and 6000 h/km^2). One sector takes waters from a higher section of the river and builds its irrigation area through two major ditches that flow from the right river side. Each one has SWTPs (TP1, TP2 and TP3) immediately close to their path.

Table 2
Landscape fragmentation trends (1991–2011) in the total administrative surface and agro-environmental Natural Park.

Metrics	Total administrative area		Natural Park	
	1991	2011	1991	2011
Number of patches	1507	2256	331	558
Mean Patch Size (ha)	23.6	15.0	53.0	30.9
Maximum Patch Size (ha)	4682.3	2696.0	1649.3	1517.5
Patchiness Variance	18,017.1	5352.0	22,553.0	9477.0
Patchiness Standard Deviation	134.2	73.2	150.2	97.4

A second irrigation sector is constructed from the dam located at the lower river Turia section, driving two main canals from the left river bank. SWTPs TP4 and TP5 are located along their courses.

A greater sector is built with waters harvested from river Júcar that contribute to the construction of most of the irrigated landscape of the study area, within which several SWTPs are scattered (TP9, TP10, TP11, TP12 and TP13). This is an area with much lower population densities, below 1000 h/km^2 in most municipalities.

The river Jucar irrigation sector also receives leftover waters from the river Magro external system. The agricultural system is completed with a small sector whose main source of water is the lake, although underground waters are also supplied to the irrigation network. As only incoming waters from rivers were examined in this study, samples from this small irrigation sector were not analysed.

Pharmaceutical target compounds varied spatially. Pharmaceuticals were detected at higher concentrations at P3, P4, P6, P9, P13 and P19 (Table 3 and Fig. 4). The highest concentrations for 7 out of the 13 detected compounds in surface water were found at site P13, not considering below MQL values. This sample point is located near of the L'Albufera South SWTP TP10. However, the high presence of pollutants and values cannot be explained by the presence in the neighbourhood of the treatment plant, as it is not connected to the irrigation channels that collect the wastewater coming from the SWTP. This point is near an industrial area with different nightclubs, and the high level of pharmaceuticals could be due to the direct spillage of sewage water into the small irrigation channels. In contrast, samples from P16, which is close to the system that drives the wastewater to the lake to maintain the ecological flow, do not show high concentrations of pharmaceuticals.

The second group of points with high concentrations and frequency of pharmaceuticals was composed of sites P3, P4, P6 and P9; this is a sector with very high population densities. In contrast, fewer substances and lower values were detected in the irrigation sector of points P1 and P2. The influence of SWTPs TP2 and TP3 is evident for the sector, with water harvested from the higher section of the Turia River supporting a true interconnection between SWTP and the irrigation network by water poured into the ditch from sewage treatment plants. For the second sector, interconnection is less evident, suggesting that water is mainly driven to the sea rather than directed to the irrigation system, although treated water is poured into the ditch, as supported by site P1.

The river Júcar area has, in general, both a lesser number of compounds detected and lower concentrations, except for point P13. Within the sector, higher values are found at sites P15 and P17, which have their irrigation network connected to SWTP TP13.

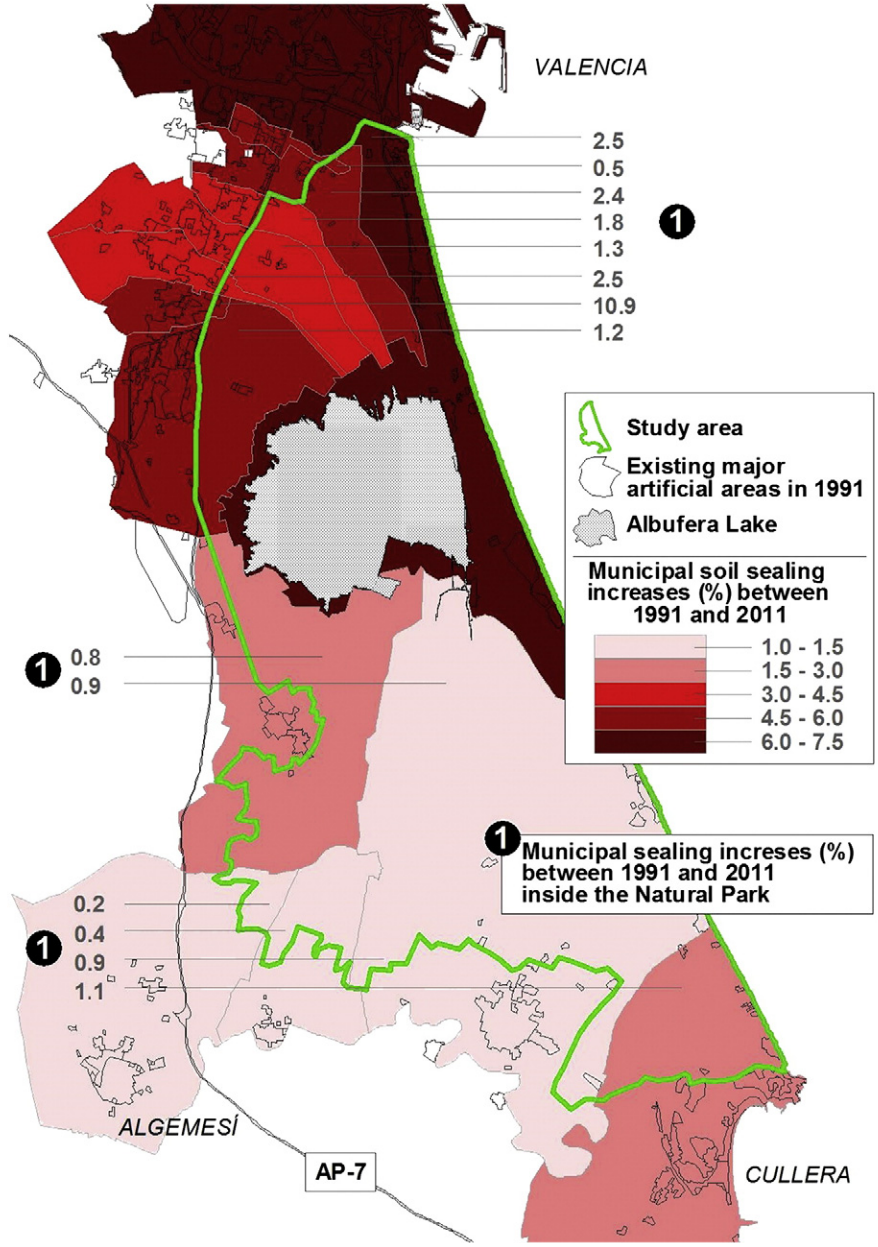

Fig. 2. Diachronic spatial representation of soil sealing trends at municipal level.

Point P20 presents a remarkable concentration of pharmaceuticals and, to a lesser degree, so does point P19, although both sites are located near TP13 SWTP. However, it is not clear why these points show this distribution pattern. As they are located close to the city of Sueca, direct spill into irrigation canals might be possible. Points P11, P12 and P14, in the north of the Júcar sector, and point P21, in the south, do not present any pharmaceuticals, as they are not inside irrigation networks connected to SWTPs.

4. Discussion

4.1. Soil sealing general dynamics and presence in the protected agro-ecological area

Land-take from nature and agriculture was considerably high in 1991 in the administrative study area. The increment of artificial surfaces must be inserted into a broader context whose dynamism has been continuous since the nineteen-fifties. Pascual Aguilar (2002) found that, between 1956 and 1997, the increment ranges from 2.5% to 17% in the 118,200 ha region in which the metropolitan area of the city of Valencia is inserted, a value quite similar to that obtained(14.9%) in 1991 for the total administrative area studied. Furthermore, artificial surfaces in the region extend along the coastline in which the study area is located, where in 1991 rates of up to 12% were found in some sectors (Añó Vidal et al., 2005; Pascual et al., 2005). The results are also similar to those obtained in other European coastal areas (European Environment Agency, 2006).

Land cover change drivers are common to other Mediterranean zones (Salvati and Zitti, 2009), with land conversion from traditional farming to artificial covers and agriculture intensification being the main agents. The higher densities may be associated with intrinsic urban dynamics that will give rise to spatial differences depending on the proximity to urbanisation axis or main city centre (Salvati, 2013). Thus, soil sealing in the northern sector is related to the increase in artificial surfaces of a larger metropolitan area entity in which the city of Valencia acts as engine of growth through outsourcing of functions

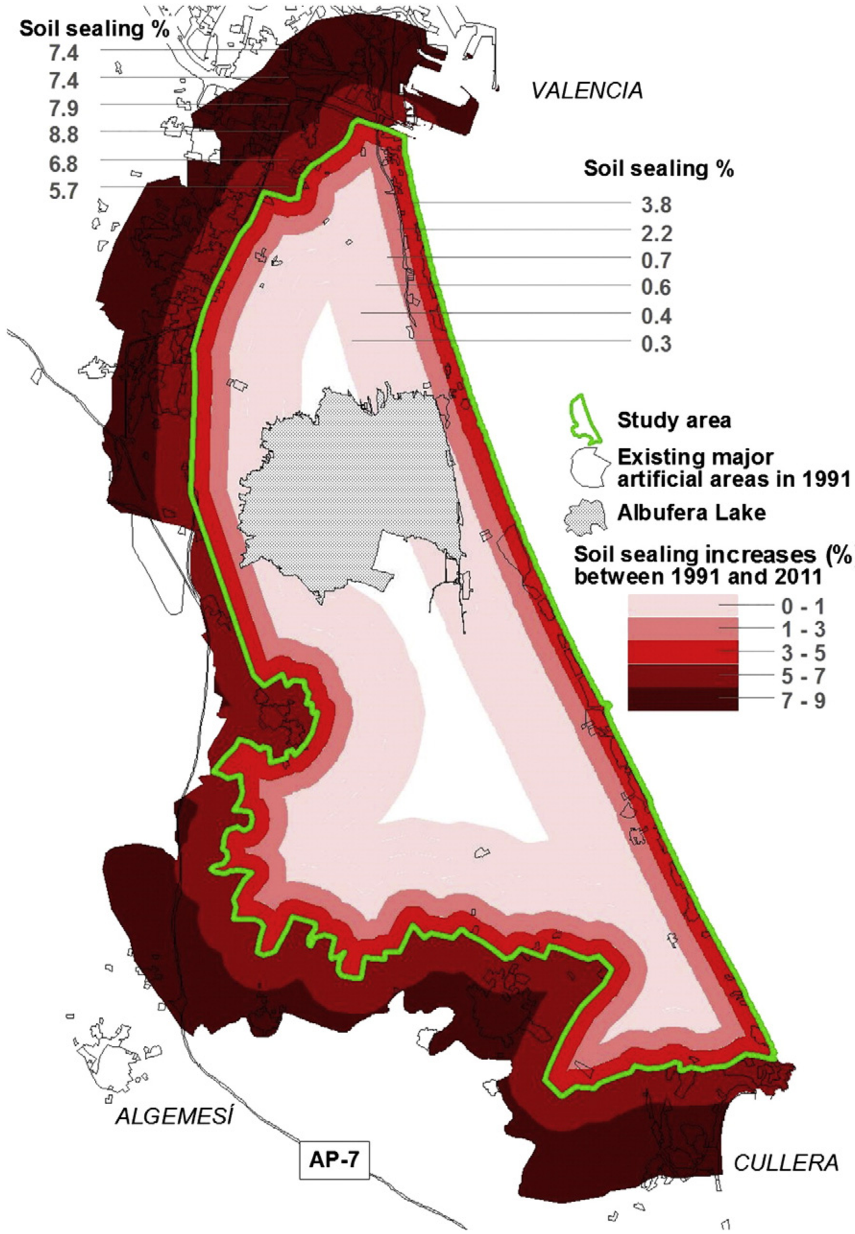

Fig. 3. Soil sealing density buffers in the protected Natural Park.

which, in turn, contributes to the expansion of neighbouring surfaces already consolidated, giving a double phenomenon of extension of the already existing land uses – neighbourhood effect – and expansion of activities to other places — spatial externalities (Hagoort et al., 2008).

Rates found are relevant as they may indicate a certain environmental impact when the artificial sealing exceeds 10%, or degradation when they are larger than 30% (Arnold and Gibbons, 1996), situation that is common, one way or another, in most of the studied municipalities in 1991 and in 2011. Environmental degradation is not only produced from soil loss imposed by artificial surfaces (Bowyer et al., 2009). Soil sealing also affects the quality of other environmental compartments (Scalenghe and Ajmone Marsan, 2009), as urban runoff from artificial covers may add dissolved pollutants in surface waters (Hope et al., 2004; Kayhanian et al., 2007).

Land degradation due to land use changes involves the interaction of the natural ecosystem and the socio-economic system (Bajocco et al., 2012), with predominance of the latter. Whenever urban activities follow continuous expansion open space landscapes will be affected by the unsustainable (economical and/or environmental) use of rural and peri-urban areas that cannot overcome the new socio-economic conditions. This is also applicable to the land of the Natural Park which is in connection to the unprotected municipal sectors, where socio-economic growth factors may impede total effectiveness of environmental policies in the protected area (Cabral et al., 2011).

4.2. Indirect identification of Pharmaceuticals in the Natural Park

With regard to most detected drugs in the study area, high presence of carbamazepine was also reported by other researchers, with mean concentrations between 1 and 794 ng/L (Conley et al., 2008; Kim et al., 2007). Acetaminophen, ibuprofen and sulfamethoxazole were detected with frequency close to 50%, but at much higher mean concentrations of 860.3 ng/L and 207.7 ng/L and 407.0 ng/L, respectively. For ibuprofen, a significant removal in SWTPs is reported in the literature (Ternes et al., 2004), and as a result of its low distribution constant value, the removal should be based on biodegradation. In general, the frequency of positive samples and mean concentration is similar to that reported by other authors (Kim et al., 2007), but differs from a

Table 3
Determination and quantification of pharmaceutical compounds. Values in ng/L.

Point	Oxytetracycline	Tetracycline	Ofloxacin	Fenofibrate	Ciprofloxacin	Norfloxacin	Codeine	Trimethoprim	Diazepam	Metoprolol	Propanolol	Sulfamethoxazole	Carbamazepine	Acetaminophen	Ibuprofen	Clofibric acid	Diclofenac
P1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10.7	6.8	26.2	<LOQ	ND	ND
P2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P3	ND	ND	49.3	ND	<LOQ	ND	68.1	53.6	5.6	5.8	6.8	139.0	24.1	ND	131.2	ND	125.6
P4	ND	ND	34.3	ND	<LOQ	ND	27.1	ND	4.6	ND	3.3	18.9	16.0	ND	34.2	ND	25.3
P5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	4.1	2.2	14.9	ND	ND	ND
P6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<LOQ	ND	15.3	ND	<LOQ	ND	ND
P7	ND	ND	<LOQ	ND	ND	ND	ND	ND	ND	ND	ND	ND	10.3	ND	<LOQ	ND	ND
P8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<LOQ	ND	ND	ND
P9	ND	ND	<LOQ	ND	ND	ND	34.7	40.5	6.0	5.6	5.9	144.0	31.0	23.1	84.3	ND	57.6
P10	ND	ND	ND	ND	<LOQ	ND	<LOQ	ND	ND	ND	ND	ND	<LOQ	249.2	ND	ND	ND
P11	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P12	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P13	ND	ND	43.9	ND	<LOQ	ND	434.0	32.5	6.3	ND	8.4	44.8	21.9	17,699.4	3913.7	71.4	260.9
P14	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P15	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<LOQ	<LOQ	25.3	21.7	42.6
P16	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	<LOQ	ND	<LOQ	ND	ND
P17	ND	ND	<LOQ	ND	ND	ND	ND	ND	ND	ND	ND	ND	3.7	18.9	<LOQ	ND	ND
P18	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	17.4	3.1	ND	ND	<LOQ	ND
P19	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	24.1	11.4	13.9	ND	ND	ND
P20	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	6.3	2.4	15.1	101.4	42.3	73.2
P21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Limits of Detection (LOD) and Method Quantification Limits (MQL)																	
LOD	9.4	10	8.1	1.8	12	9.6	1.2	0.9	0.3	1.2	0.6	0.9	0.6	0.9	4.8	1.5	2.5
MQL	28.2	30	24.3	5.4	36	28.8	3.6	2.7	0.9	3.6	1.8	2.7	1.8	2.7	14.4	4.5	7.5

few studies that only found some traces below the MQL (Gros et al., 2006; Kasprzyk-Hordern et al., 2008).

Summarising, higher concentrations of the pharmaceuticals and drugs of abuse detected were mainly found in the sites located in ditches whose irrigation networks are connected to SWTP outflows. This distribution is reasonable because the main sources of these substances are effluents from sewage treatment plants. This connection suggests a larger landscape and environmental compartments structure in which hydrological connectivity allows transport of non desirable substances (Pringle, 2003).

In a connectivity framework like this, contaminants will be released into the agricultural environment though the irrigation network (it could also occur by application of bio solids or other solid waste materials obtained from SWTPs) to soil, as stated by Saccà (2010). Contaminants may degrade and disappear with time, or else infiltrate and percolate into deep water layers (Cabeza et al., 2012).

The presence of emerging contaminants highlights the need to implement different treatments other than those conventionally used in SWTPs, such as the one reported by Cabeza et al. (2012), with treatment by ultrafiltration reverse osmosis and UV disinfection. Once contaminated water enters the agricultural system, some dissemination mechanisms should be considered related to both human health and environmental risk. Persistence and accumulation in agricultural soils of the study area should be of major concern, as soils may have a storage capacity that would allow residence time and accumulation of contaminants when irrigated with waste waters (Chen et al., 2011).

Some compounds persist for months after irrigation, and accumulate in soil which, together with new supplies from incoming irrigation waters, will establish potential human exposure pathways through ingestion of food plants cultivated on land irrigated with waste waters (Weber et al., 2006). Although plant uptake values for emerging contaminants have been established, studies of this kind are very scarce and based on experimental trials (Jones-Lepp et al., 2010) and/or indirect estimations (Calderón-Preciado et al., 2011).

One of the major concerns in the study area is the environmental impact produced on the Natural Park. So far, very little is known about the ecotoxicology of emerging contaminants for wild species. Effects on biota may be related to the chemical properties of the contaminants. Exposure of *Pimephales promelas* results in reproductive disruption due to endocrine-active chemicals in the SWTP effluent (Vajda et al., 2011). The fact that most of these residues still have potent activities constitutes a justifiable motive to presuppose that their regular presence in distinct hydrological and environmental compartments will have potential implications for wildlife and human health (Jones-Lepp et al., 2004). The regular presence of these substances in water samples could entail consequences for aquatic and terrestrial organisms, particularly in ecosystems (such as the study area) that are the last reservoirs of several autochthonous species and a key stopover point for migratory birds.

5. Conclusions

Anthropogenic soil sealing increase has occurred in all territorial units (municipalities and Natural Park) analysed. Between 1991 and 2011, land-take reached 18.6% for the total administrative area, although it was relatively high in 1991 (14.9%). There was an increase of 1.4% in the Natural Park in the 20 year period under study. In 2011 soil sealing reached 5.2% of the protected land.

The enlargement of artificial surfaces has caused an increment of soil fragmentation in the study zones. It is characterised by the reduction of the maximum and mean patch size, and the homogenisation of the patch size reflected by the reduction of the patch variance and standard deviation.

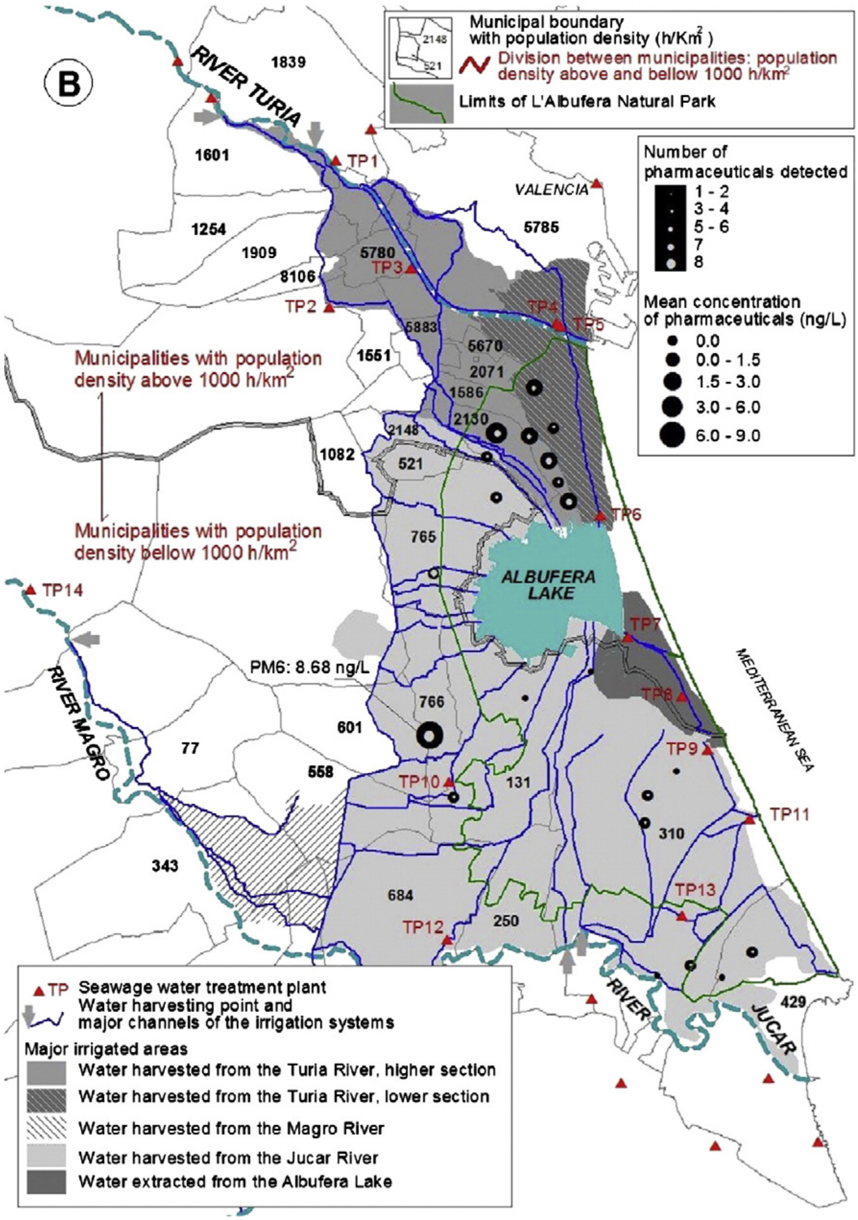

Fig. 4. Trends and spatial significance of pharmaceuticals.

The constant increase in artificial surfaces may be seen as a relevant direct factor of land use/cover change in the study area. It is included in a larger structure (at least to metropolitan scale) that has long continuity in time. Neighbouring and externalisation are processes that would explain the greater incidence of artificialisation in Northern municipalities and the penetration in the outer 1000 m stripe of the Natural Park.

A large number of pharmaceuticals (13 out of 17) were detected in surface waters. Of the 21 monitored sites, they were quantified at 16 points. Number of compounds and concentrations varies among sites. Higher amounts of analytes were found in P13 (with a total of 12 compound), P3 and P9 (11 compounds) and P4 (9 compounds). Trends in detected substances are also found, with carbamazepine, ibuprofen, acetaminophen and sulfamethoxazole being the compounds most frequently detected (found in 15, 11, 10 and 9 samples respectively). As none of the samples were collected at the direct outflows of SWTPs, the presence of pharmaceuticals indicates connections between hydrological compartments or water flow paths between environments.

The spatial incidence and trend of contaminants refer to four patterns: (1) larger number of contaminants and higher concentrations detected, which will be in sectors with very high population densities and urban water from SWTPs linked to irrigation networks (P3, P4, P6, P7 and P9); (2) sites with some contaminants in smaller concentrations detected that are linked to SWTPs in municipalities with lower population density (less than 500 h/km^2); (3) sites which, by their higher concentration and number of compounds detected, may point to direct spill into the irrigation network as suggested by P13; and (4) sites without any compound detected and located in areas without connection between urban waters and the Natural Park (P12, P11 and P14).

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