Science of the Total Environment 955 (2024) 177286

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Evaluation of the atmospheric pollution by pesticides using lichens as biomonitors

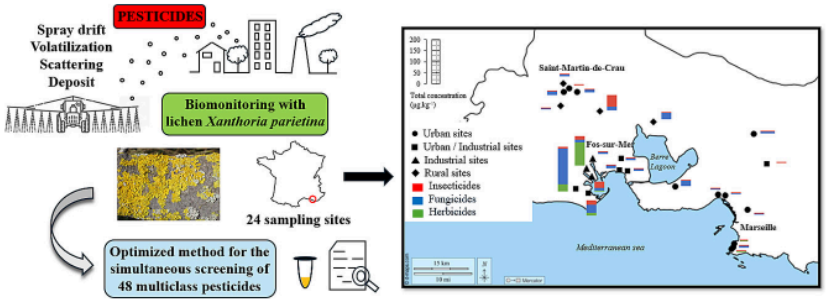
Amandine Durand [a,*], Julien Dron [b], Pascale Prudent [a], Henri Wortham [a], Caroline Dalquier [b,c], Mathilde Reuillard [b], Annabelle Austruy [b]

[a] Aix Marseille Univ, CNRS, LCE, Marseille, France
[b] Institut Écocitoyen pour la Connaissance des Pollutions, Fos-sur-Mer, France
[c] Université de Lorraine, INRAE, LSE, F-54000 Nancy, France

HIGHLIGHTS

- Lichens can be used to monitor the atmospheric exposure to pesticides.
- Reliable method for simultaneous screening of 48 pesticides was developed.
- 15 pesticides, including 4 banned, detected in all 24 sites of southern France.
- 13 detected pesticides considered as priority active substances in air monitoring.
- Lichen biomonitoring revealed possibly high contamination of industrial areas.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Philip Hopke

Keywords:
Biomonitoring
Air pollution
Xanthoria parietina
Bioaccumulation
Herbicides
Analytical development

ABSTRACT

The extensive use of pesticides combined with their persistence in the environment requires new methodologies to assess more effectively the population exposure to pesticides via air pollution. Biomonitoring pesticides with lichens has been poorly documented, although it represents a complementary approach to the usual active samplings, with an exposure to pesticides accumulated and integrated over several months. An optimized extraction procedure from the lichen *Xanthoria parietina* followed by a gas chromatographic-tandem mass spectrometric analysis is proposed here to quantify simultaneously 48 pesticides considered in France as priority active substances to monitor in the air. This method has been applied to lichen samples collected in 24 sites in southern France covering urban, industrial, and agricultural areas in order to identify potential contrasts related to anthropogenic activities. Fifteen pesticides (six fungicides, five insecticides, and four herbicides), including four active compounds currently banned by EU legislation, were detected in at least one site. Lindane, diflufenican, difenoconazole, and boscalid were the most common pesticides found in all sites. Urban sites appeared generally less contaminated compared to industrial and rural ones, but a strong heterogeneity was noticed between locations. The biomonitoring with lichens revealed unexpected contaminated areas, partly due to the use of herbicides for vegetation control in industrial and railway installations. The spatial distribution also suggests an input of pesticides by atmospheric transport at the local and regional scales.

* Corresponding author.
E-mail address: amandine.durand@univ-amu.fr (A. Durand).

https://doi.org/10.1016/j.scitotenv.2024.177286
Received 18 July 2024; Received in revised form 4 October 2024; Accepted 27 October 2024
Available online 2 November 2024
0048-9697/© 2024 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

In 2022, according to the most recent statistics on agriculture, forestry, and fisheries in the European Union (UE), the total quantity of pesticide sales amounted to 322,000 tons with a major use of fungicides (43 %) and herbicides (35 %). Contrary to the general decline of pesticide sales observed in the UE between 2011 and 2022, France saw an increase in active ingredient use in the same period and registered the highest volume sold in 2022 (67,800 tons), making it the largest consumer of pesticides among EU member states (Eurostat, 2024). Despite their benefits for crop yield, the intensive and widespread use of pesticides raises concerns due to the contamination of natural resources and their possible effects on human health (Damalas and Eleftherohorinos, 2011). Chronic exposure to pesticides is considered as a risk factor for developing diseases such as non-Hodgkin lymphoma, multiple myeloma, prostate cancer, Parkinson's disease, cognitive disorders and respiratory impairments (Inserm, 2022). Depending on their application, only a minor fraction of the applied pesticides reaches their targets (Pimentel and Burgess, 2012; Zivan et al., 2017), while the remaining ends up on soil, surface waters or in the atmosphere and is thereafter dispersed through several processes including volatilization, wind erosion, leaching or runoff (Fenner et al., 2013). Studies have shown that pesticide drift may account for a few percent to 25 % of pesticide loss during spraying in agricultural areas (Tudi et al., 2021). In addition, volatilization may represent a major pathway of mass transfer from soil or plants to the atmosphere, accounting for 2 to 90 % of the applied dose (Bedos et al., 2002). Although there is currently no regulation controlling pesticides in the atmosphere, their monitoring appears necessary to provide a greater knowledge about their occurrence in the environment, to understand their fate and partitioning and characterize organism exposure levels. To this purpose, an interesting tool is offered by using lichens as biomonitors (Abas, 2021; Blett et al., 2003). Lichens are organisms resulting from a symbiotic association of a fungus and a chlorophyll-containing partner, either algae or cyanobacteria (Nash, 2008). Lichens receive all their nutrients and water from wet and dry atmospheric deposition, which makes them very sensitive to air pollution and thus valuable as air quality indicators (Conti and Cecchetti, 2001; Nimis et al., 2002; Ratier et al., 2018). Their wide geographical distribution and abundance allow studies over a large area with a low-cost sampling procedure and minimal materials required. Lichens accumulate pollutants in their pseudo-tissues during at least several months or years of exposure (Dron et al., 2021; Loppi and Paoli, 2015) constituting a complementary approach to the usual methods favoring active sampling of air over a period of a few dozen hours (Yusà et al., 2009).

The determination of various pollutants in lichen pseudo-tissues can yield valuable information about their occurrence in the environment. Many studies have already been conducted to monitor metals with lichen pseudo-tissues (Garty, 2001; Nimis et al., 2001; Parzych et al., 2016; Ratier et al., 2018). For organic compounds, biomonitoring studies using lichens are scarce and mainly focus on polycyclic aromatic hydrocarbons, (Augusto et al., 2010; Dron et al., 2021; Ratier et al., 2018; Studabaker et al., 2017; Van der Wat and Forbes, 2019), polychlorinated biphenyls (Herzig et al., 2019; Ratier et al., 2018), dioxins and furans (Augusto et al., 2007, 2016; Ratier et al., 2018) and markers of biomass burning (Dauphin et al., 2020). Regarding pesticides, to our knowledge the few studies reported mainly focused on organochlorine pesticides (Herzig et al., 2019; Schrlau et al., 2011; Villeneuve et al., 1988; Zhu et al., 2015) and glyphosate (Lucadamo et al., 2018; Vannini et al., 2016). The determination of pesticides in lichens is technically challenging because concentrations are expected to be low and natural substances, *eg.* issued from lichen pseudo-tissues, can interfere with the targeted compounds during the spectrometric analyses. An optimized method for the simultaneous screening of 48 pesticides, mostly currently used or recently banned substances, in lichen samples is proposed here. This method was validated and subsequently applied to real lichen samples collected in 24 sites across the Aix-Marseille-Provence metropolitan area (south of France), characterized by the presence of numerous and diversified anthropogenic activities. The objectives of this study were to (1) investigate the occurrence of pesticides in the atmosphere in this area using lichen biomonitoring, (2) evaluate if lichens are relevant to biomonitor pesticides in contrasted environments influenced by various anthropic activities.

2. Materials and methods

2.1. Study area

Sampling sites were located in southern France, between the Rhône delta and the Marseille urban area. This region, Aix-Marseille-Provence metropolitan area, is one of the most densely populated in France, hosting around 2 million people (INSEE, 2021). The high density of industries, maritime activities, human infrastructures, and agricultural activities make this territory prone to high pollution levels. Agricultural areas cover 26 % of the territory, with an activity mainly oriented towards arboriculture, market gardening, and viticulture. Sites were specifically chosen for their different context of human activities in order to form a representative panel of exposure to pesticides in the study area. To establish this selection, the area was meticulously characterized in terms of land use and anthropic activities based on the national databases available on polluted sites and soils, pollutant emissions, pesticide sales, and cadastral data (Austruy, A., 2022). Sites were categorized as urban, industrial or rural areas based on the surrounding dominant land use. Marseille (pop. 873,076) and Aix-en-Provence (pop. 147,478) are the two largest cities of the area (INSEE, 2021). Gardanne (pop. 21,124) and Châteauneuf-les-Martigues (pop. 17,909) are part of the Aix-en-Provence – Marseille urban agglomeration and are close to vegetable and cereal crops. Fos-sur-Mer (pop. 15,469) is the main maritime industrial zone in France including a vast petrochemical complex, various industries (steel, energy, chemistry, urban and industrial waste incineration units) and world-leading maritime terminals (containers, ore, oil, gas, cereal). Port-Saint-Louis-du-Rhône is also an industrial town (pop. 8,446) with important maritime and petrochemical activities. It is also known for its many marshes and an agricultural production towards rice farming and cereals. Saint-Martin-de-Crau (pop. 13,729) is a rural town with wide natural areas with more than 17,000 ha of protected steppes dedicated to the cultivation of “Crau hay” (Registered Designation of Origin) and orchards. It also has surfaces allocated to market gardening and the production of olives, nuts, and cereals. Finally, Cornillon-Confoux (pop. 1,571) is a rural town with nearly 55 % of its land dedicated to agricultural activities, mainly the cultivation of vegetables, fruits, viticulture, and field crops. A total of 24 sampling sites including 11 urban sites, 6 urban/industrial sites, 3 industrial sites and 4 rural sites were selected and are presented in detail in Table 1. Highly populated areas were prioritized, as shown by the selection of a majority of urban sites, due to the sanitary concerns surrounding pesticide use.

The climate is Mediterranean with mild winters and warm, dry summers. According to data from the meteorological station of Marseille-Marignane (Météo-France, 2021) during the six months preceding the sampling, the mean temperature was 20.6 °C with 1,774 h of sunshine and a total of 234 mm rainfall. Northwesterly winds dominate in this region (approx. 40 %), but winds from the southeast and the east may also contribute up to 25 % in summer when sea-breeze conditions are frequently observed (Ratier et al., 2018; Dron et al., 2021).

2.2. Field samplings

Lichen samples were collected from October 4 to 15, 2021. For consistency and to allow comparison between sites, collection was performed during the shortest possible period so that sampling was representative of homogeneous environmental conditions. It has been shown that the bioaccumulation of very different contaminants such as

Table 1
Exact locations of the 24 sampling sites (WGS84 coordinates), their type (U: Urban; UI: Urban/Industrial; I: Industrial; R: Rural;) and their characteristics.

Site Name	Location	Latitude (°N)	Longitude (°E)	Type	Description
AIX	Aix-en-Provence	43.519823	5.449357	U	Urban park
CHF	Châteauneuf-les-Martigues	43.390106	5.156074	U	Urban area near market gardening
MN1	Marseille (north)	43.363657	5.327305	U	Urban park, near railroad
MN2	Marseille (north)	43.365753	5.309998	U	Urban park close to the coast
MRS	Marseille (center)	43.326250	5.400930	U	Urban park
MS1	Marseille (south)	43.239063	5.367627	U	Urban park near the Calanques National Park
MS2	Marseille (south)	43.229105	5.354494	U	Natural area in the Calanques National Park
MS3	Marseille (south)	43.231481	5.360910	U	Urban residential area near the Calanques National Park
SME	Saint-Martin-de-Crau	43.636588	4.827686	U	Urban park near major road
SMN	Saint-Martin-de-Crau	43.643431	4.808055	U	Urban residential area near organic cereal farming
SMO	Saint-Martin-de-Crau	43.635539	4.791997	U	Urban park near golf course
ENG	Fos-sur-Mer	43.431389	4.974244	UI	Urban residential area near ponds and chemical industry
FOA	Fos-sur-Mer	43.433084	4.947911	UI	Urban park near ponds and major road
FOM	Fos-sur-Mer	46.463835	4.947756	UI	Urban park near industrial area
GAR	Gardanne	43.454223	5.465259	UI	Urban area near chemical industry
PSL-S3	Port-Saint-Louis-du-Rhône	43.396682	4.803336	UI	Urban park near market gardening
PSL-S10	Port-Saint-Louis-du-Rhône	43.386845	4.850011	UI	Coastal area
CAB	Fos-sur-Mer	43.439625	4.839973	I	Natural area near chemical, energy industries and railway
GOU	Fos-sur-Mer	43.417650	4.860107	I	Natural area near chemical industries and incinerator
TON	Fos-sur-Mer	43.459677	4.851368	I	Natural area near energy companies and chemical industries
COR	Cornillon-Confoux	43.566907	5.070480	R	Park near sport field
CPH	Saint-Martin-de-Crau	43.654700	4.790452	R	Park near Crau hay prairies
ENT	Saint-Martin-de-Crau	43.599995	4.896676	R	Natural area near orchads
TNT	Saint-Martin-de-Crau	43.612968	4.785948	R	Natural area near Crau hay prairies and pasture

PAHs and metals in the lichen *Xanthoria parietina* is representative of the atmospheric exposure over several months to 1 year, possibly more according to the exposure and climatic conditions (Augusto et al., 2009; Dron et al., 2021; Paoli et al., 2018; Zhao et al., 2019). Regarding the sampling period, and assuming that the studied pesticides show a comparable integration time, this integration time would cover spring and summer, when pesticides are predominantly applied. *X. parietina* is a ubiquitous and pollution-tolerant lichen specie, which can be found in rural, urban, and industrial areas. It is the most widely used lichen species in European bioaccumulation programs (Nimis et al., 2001) and the most represented in the study territory (Austruy, 2022). On each sampling site, *X. parietina* full thalli (> 3 cm diameter) were collected on at least 5 trees at a height of 1.2 to 2.5 m to minimize the influence of soil resuspension. The trees were selected at least 100 m away from potentially strong emission sources (high-traffic roads, cultivated fields, industrial installations, etc.), to ensure an exposure to diffuse atmospheric pollution and that lichens were in sufficiently good conditions. Visual control was also realized to discard necrotic lichen thalli from sampling. The lichen thalli were pulled off the tree bark using ceramic knives and stored away from light at 4 °C until preparation, which was done within 24 h. After removing unwanted materials (remaining bark, other lichen species, dust…), they were freeze-dried and finely ground in a ball mill equipped with ZrO_2 beads and capsules. The samples (approximately 1 g) were then stored at −45 °C until analysis.

2.3. Pesticides selection

The selection of pesticides was based on monitoring conducted by the Observatory for Pesticide Residues in the region Provence-Alpes-Côte-d'Azur region, France (ORP PACA) between 2012 and 2017 (Désert et al., 2018). Pesticides were chosen according to their regional sales quantity, their toxicity, their occurrence in the atmosphere and their suitability to the analytical method. A total of 48 active substances were chosen including 20 herbicides, 17 fungicides and 11 insecticides among which is an insecticide synergist (Table S1). The French Agency for Food, Environmental and Occupational Health & Safety (ANSES) classified 34 of these substances as priority active molecules to monitor in ambient air in France (Hulin et al., 2021). Among them, some are banned for years (e.g. lindane was prohibited in France for agricultural uses in 1998) but regarding their persistence in the environment, they can still be found in quantifiable concentrations (Désert et al., 2018).

2.4. Chemicals

Pesticide standards (purity >95 %) were purchased from Sigma-Aldrich (PESTANAL, analytical standard). Triphenyl phosphate (TPP; purity >99 %) was used as an internal standard and was purchased also from Sigma-Aldrich. A stock solution of each pesticide was prepared by dissolving the pure standard in dichloromethane (DCM) or acetonitrile (ACN). Standard mixed solutions were then prepared by diluting the stock solutions with ACN. Both the stock and working solutions were stored at −18 °C. All solvents used were of analytical grade and obtained from Sigma-Aldrich.

2.5. Chemical extraction and cleanup optimization

Accelerated Solvent Extraction (ASE 350, Dionex) was carried out to extract pesticides from the lichen samples. Approximately 0.5 g of lichen powder was precisely weighted and spiked with 20 µL of a 5 $mg.L^{-1}$ TPP solution before being introduced into the middle of a 66 mL stainless-steel cell filled with glass beads (VWR). Glass fiber filters (Thermo Scientific) covered both the top and the bottom of the cell. Two solvents were tested for the extraction, DCM and ACN, chosen for their ability to dissolve pesticides. The other extracting conditions were: temperature, 100 °C; pressure, 100 bars; heat up time, 5 min; static time, 5 min; flush volume, 70 % of the extraction cell volume; purge time, 300 s. Four

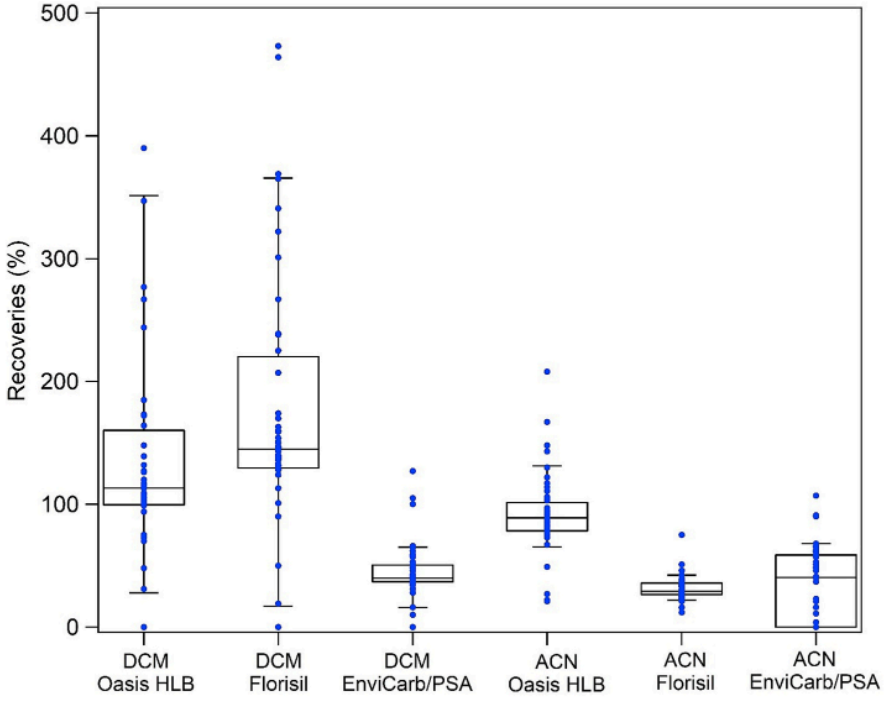


Fig. 1. Recoveries (%) comparison between different combinations of extraction solvents and clean-up sorbents on a lichen matrix spiked with pesticides. Each experiment was conducted in 3 replicates. Each point represents the average of the 3 replicates for each individual pesticide. At this stage, concentrations were not corrected by the internal standard. DCM: dichloromethane, ACN: acetonitrile.

cycles per cell were carried out to maximize the extraction recoveries. Extracts were reduced under a nitrogen stream at 40 °C (TurboVap II, Biotage) until reaching a volume of 5 mL. They were then purified using a Solid Phase Extraction (SPE) cartridge. The efficiency of three solid phases was compared: Florisil 500 mg (Sigma-Aldrich), Oasis HLB 150 mg (Waters) and Supelclean ENVI-Carb II 500 mg/PSA 300 mg (Sigma-Aldrich). The cartridge sorbent was initially conditioned with 6 mL of the extraction solvent (DCM or ACN). The extract was then slowly loaded and recovered in a clean vial after passing through the solid phase. The cartridge was rinsed with 6 mL of the extraction solvent, which was also recovered and added to the purified extract. The sample was then concentrated under a gentle N_2 stream at 40 °C to a volume of 500 µL, and finally filtered through a 0.45 µm PTFE syringe filter (Sigma-Aldrich). The extracts were conserved at −18 °C until analysis.

2.6. Sample analysis by gas chromatography – Mass spectrometry tandem (GC–MS/MS)

Sample analyses were performed with a Trace GC Ultra (Thermo Scientific) coupled to a TSQ Quantum Triple Quadrupole (Thermo Scientific) operated in the electron impact ionization mode (70 eV). Most of the conditions were derived from a previous work carried out on atmospheric samples (Désert et al., 2018): column, TG-5MS (30 m*0.25 mm*0.25 µm, Thermo Scientific); carrier gas, helium at a constant flow rate of 1 mL.min^{-1}; splitless injector, splitless time of 2 min with surge pressure of 300 kPa during 2 min; injection volume, 1 µL; inlet temperature, 250 °C; transfer line temperature, 250 °C; oven temperature program, hold 2 min at 35 °C, then increased to 180 °C at a rate of 25 °C.min^{-1}, and finally increased to 300 °C at 5 °C.min^{-1}, which was held for 3 min. The ion source temperature was fixed at 250 °C. The MS was operated in multi reaction monitoring mode (MRM) using argon as collision gas at 1 mTorr. Transitions used to identify and quantify each pesticide are given in Table S2. Peaks were positively identified in correspondence with the retention time of the standard compound and considering that the intensity ratios of MRM transitions matched with those of the standards (Fig.S1).

2.7. Method validation

The recoveries of individual pesticides were determined by spiking known amounts of pesticides (0.25 µg) into a dry and ground lichen sample (0.5 g). Additionally, the linearity of the method was assessed by spiking a lichen matrix with known increasing quantities of pesticides (0.01; 0.02; 0.1; 0.25; 0.375 µg). Repeatability of the method was evaluated by determining the relative standard deviations (RSD) from 12 spiked replicates in lichen from 3 different sampling sites. The limits of detection (LODs) and quantification (LOQs) were calculated using the signal-to-noise ratio approach. Lichen matrix was spiked with known low concentrations of pesticides and the minimum concentration at which analytes could be reliably detected and quantified (signal-to-noise ratio of 3:1 and 9:1 respectively) were determined. As there is no commercially available certified pesticide-free lichen material, lichen used as a matrix was collected from an area with a low expected exposure to pesticides and was initially analyzed without additional substances to determine the initial pesticide content. The pesticides were either undetectable or found in negligible concentrations compared to the spiked quantities. The final method was then applied to a certified reference material (CRM) of wheat flour (ERM-BC706, European Commission's Joint Research Centre). This CRM was certified for the content of 7 pesticides targeted in this study in a vegetable matrix and was the most suitable reference material commercially available to assess the accuracy of the method.

3. Results and discussion

3.1. Method development

The selection of an appropriate extraction solvent plays a decisive role in achieving optimal extraction recoveries of pesticides. ACN and DCM were chosen for their efficiency in extracting a wide range of polar

Table 2
Results obtained for the validation of the analytical method (recovery, reproducibility, linearity, limits of detection and quantification), and for the analysis of the CRM ERM-BC706 (mean of 4 replicates). The results of these experiments include internal standard (TPP, triphenyl phosphate) correction.

Pesticide	Recoveries	RSD	Linearity R^2	LOD	LOQ	CRM conc calculated	CRM conc certified
	%	%	–	$\mu g.kg^{-1}$	$\mu g.kg^{-1}$	$\mu g.kg^{-1}$	$\mu g.kg^{-1}$
Aclonifen	103	30	0.999	31	93		
Chlorpropham	114	18	0.995	16	48		
Clomazone	94	15	0.990	0.3	0.9		
Diclofop-methyl	82	12	0.993	8	24		
Diflufenican	92	13	0.994	0.2	0.5		
Dimethenamid-P	92	16	0.992	0.3	0.9		
Flazasulfuron	91	11	0.972	3	9		
Flumioxazin	163	50	0.993	0.3	0.9		
Flurochloridone	85	13	0.992	16	48		
Isoproturon	64	15	0.977	1.6	4.8		
Lenacil	106	21	0.993	31	93		
Linuron	76	17	0.987	16	48	0.52 ± 0.07	0.51 ± 0.06
Metazachlor	87	14	0.994	1.6	4.8		
Oxadiazon	88	14	0.992	31	93		
Pendimethalin	101	18	0.993	2	6		
Propyzamide	89	17	0.993	3.1	9.3		
Prosulfocarb	89	14	0.982	8	24		
S-metolachlor	94	13	0.994	2	6		
Terbuthylazine	99	22	0.983	1.6	4.8		
Triallate	87	16	0.988	16	48		
Boscalid	113	34	0.991	0.3	0.9		
Cyprodinil	88	15	0.991	3	9		
Difenoconazole	166	48	0.988	0.3	0.9		
Dimethomorph	163	40	0.987	1.6	4.7		
Epoxiconazole	85	17	0.990	8	23		
Fenhexamid	136	29	0.994	1.6	4.8		
Fenpropimorph	82	16	0.991	1.6	4.8		
Fluazinam	42	14	0.981	160	500		
Flusilazole	94	22	0.997	16	48		
Folpet	29	9	0.997	160	500		
Iprodione	101	24	0.992	3	9		
Kresoxym-methyl	100	13	0.991	31	93		
Pyrimethanil	93	11	0.999	3	9		
Spiroxamine	97	27	0.992	16	48		
Tebuconazole	98	14	0.994	2	6	0.035 ± 0.008	0.041 ± 0.006
Tetraconazole	90	16	0.986	0.3	0.9		
Tolylfluanid	38	22	0.983	160	500		
Chlorpyrifos	91	14	0.995	0.3	0.9	2.42 ± 0.50	2.43 ± 0.23
Chlorpyrifos-methyl	91	12	0.995	16	48		
Cypermethrin	108	15	0.989	0.3	0.9	4.9 ± 0.7	3.7 ± 0.5
Deltamethrin	115	30	0.988	2	6	4.0 ± 0.6	3.8 ± 0.7
Fenoxycarb	95	15	0.996	16	48		
Fipronil	84	11	0.993	1.6	4.8	0.42 ± 0.05	0.42 ± 0.04
Lambda-cyhalothrin	92	20	0.990	16	48		
Lindane	83	13	0.987	0.3	0.9		
Permethrin	100	21	0.993	31	93	0.48 ± 0.06	0.40 ± 0.07
Piperonyl butoxide	107	20	0.995	31	93		
Pirimicarb	89	16	0.993	8	24		

and nonpolar compounds. Considering the high organic matter content in lichen samples, a clean-up step was deemed necessary and the Oasis HLB, Florisil, and EnviCarb/PSA sorbents were tested. Extraction with DCM led to co-extracted matrix components which were not efficiently removed during the clean-up step either with the Oasis HLB or the Florisil sorbents. The enhancement of the chromatographic signal due to the matrix effects resulted in excessively high recoveries above 130 % for 14 and 36 pesticides (among the 48 targeted) using the Oasis HLB and Florisil cartridges, respectively (Fig. 1). The matrix-induced signal enhancement is frequently observed during pesticides analysis of samples containing complex matrix components (e.g. lipids, pigments, resins, sugars, etc.) (Erney et al., 1993; Poole, 2007). The injection port of the GC is composed of active sites which are mainly free silanol groups present in the glass liner. The accumulation of non-volatile components originating from repeated analyses of samples may also result in the formation of active sites in the injector or in the first centimeters of the GC column. When the analytes prepared in pure solvent are injected, they may bind to these active sites, resulting in their incomplete transfer to the detector. However, when the same amount of analytes in a real sample is injected, the matrix components, typically the most abundant components of the sample in trace analysis, compete with the analytes to react with the active sites hence reducing losses during the injection. Therefore, overestimated concentrations may be achieved. Polar pesticides and pesticides with high molecular masses (> 400 $g.mol^{-1}$) are more likely affected by matrix effect (Sánchez-Brunete et al., 2005). Jiménez et al. (1998) reported recovery percentages >1000 % for certain pesticides such as parathion and folpet in honey matrices.

The EnviCarb/PSA sorbent appeared to be the most effective in removing matrix components, in particular chlorophyll compounds, sugars, and fatty acids but a significant fraction of the pesticides was also retained on the sorbent and was not eluted with either of the solvents tested. More than half of the molecules showed recoveries below 60 % (Fig. 1). Extractions performed with ACN followed by a clean-up step using an Oasis HLB cartridge provided satisfactory recoveries within 70–130 % for 39 pesticides (Table 2). Fluazinam, folpet and tolylfluanid showed poor recoveries at the concentration tested (around 23 %), but the spiked concentration was below the limit of quantification of the GC–MS/MS for folpet which may explain this result for this compound.

Table 3
Summary of results from reported studies using lichens as biomonitors of pesticides in the atmosphere.

Location	Sampling date	Lichen species	Pesticides	Extraction method	Clean-up step	Analysis method	Recovery	LOD	Mean concentration detected	Reference
Southern France	May 1986	*Usnea barbata*	11 organochlorine pesticides including lindane	Soxhlet extraction hexane	Florisil	GC-Electron Capture Detector (ECD)	Not reported	Not reported	Site1: 130 μg.kg^{-1} Site 2: 24 μg.kg^{-1}	Villeneuve et al. (1988)
United States - National parks	Summer 2004	*Letharia vulpina Xanthoparmelia Alectoria sarmentosa Platismatia glauca Masonhalea richardsonii*	65 semi-volatile organic compounds including lindane, chlorpyrifos, triallate and S-metolachlor	ASE extraction DCM	Water extraction and silica SPE	GC–MS	68 % (mean)	0.1658 μg.kg^{-1} (lindane) 0.3208 μg.kg^{-1} (triallate) 0.2521 μg.kg^{-1} (chlorpyriphos)	1.74–10.06 μg.kg^{-1} (lindane) 1.71–2.25 μg.kg^{-1} (chlorpyrifos)	Schrlau et al. (2011)
China -Tibetan Plateau	June 2010 and 2011	*Usnea longissima*	28 organochlorine pesticides including lindane	ASE extraction hexane/acetone (3:1)	Silicagel/alumina and C18 SPE	GC–MS	73 % (mean)	0.57–17 ng.kg^{-1}	0.15–1.3 μg.kg^{-1} (lindane)	Zhu et al. (2015)
Switzerland	1995 and 2014	*Parmelia sulcata*	30 organochlorine pesticides including lindane	Soxhlet extraction hexane/acetone (2:1)	Aluminum oxide and florisil	GC-High Resolution Mass Spectrometry (GC/HRMS)	39 % (13C lindane)	0.0625 μg.kg^{-1} (lindane)	12.74 μg.kg^{-1} in 1995 0.95 μg.kg^{-1} in 2014 (lindane)	Herzig et al. (2019)
Southern France	October 2021	*Xanthoria parietina*	48 pesticides (20 herbicides, 17 fungicides, 11 insecticides including lindane)	ASE extraction ACN	Oasis HLB	GC–MS/MS	90 % (mean) 83 % (lindane)	0.3 μg.kg^{-1} (lindane) 160 μg.kg^{-1} (highest value)	1.9 μg.kg^{-1} (lindane) 1.4 μg.kg^{-1} (chlorpyrifos)	This study

Finally, the Florisil clean-up of ACN extracts gave lower recoveries (31 % in average) than the Oasis HLB (90 % on average). According to these results, ACN was selected for its high ability to extract the pesticides while minimizing the amount of coextracted undesirable compounds and the Oasis HLB was shown to offer the best performances in terms of clean-up efficiency (Table S3).

3.2. Method validation

The accuracy of the method was evaluated using the certified reference material ERM-BC706, which includes certified concentrations for cypermethrin, deltamethrin, fipronil, linuron, permethrin, tebuconazole, and chlorpyrifos. Good agreement with the certified values was found for all compounds using the developed method, which is demonstrated by the measurement deviations, all included within the certified measurement uncertainty intervals. All pesticides exhibited good linearities in the studied range with regression coefficients higher than 0.99 for most of the compounds analyzed (Table 2). The reproducibility of the method was satisfactory, considering the nature of the analyzed matrix, with RSD < 30 % for 45 out of 48 compounds. Higher RSDs were found only for the three pesticides that presented recovery rates around 160 %. It can be assumed that these compounds were subjected to matrix effects inducing higher variations in the chromatographic peak areas. Finally, the LOQ values ranged from 0.6 μg.kg^{-1} (diflufenican) to 500 μg.kg^{-1} for fluazinam, folpet and tolylfluanid for which lower recoveries were previously identified (Table 2). The validated method proposed here demonstrates significant improvements in recovery rates compared to previous studies (Table 3). The discrepancies observed for the detection limits may be attributed to variations in detector sensitivity and differences in the calculation methods used, which were not detailed in the previous studies. Although there is a consensus in the definition of the LOD, there is not an agreement in the way to calculate this parameter. For instance, the determination of the LOD considering the matrix may increase the values by several orders of magnitude compared to those obtained with standards solutions.

3.3. Occurrence of pesticides in field samples

The lichens collected in the 24 sites were analyzed in accordance with the previously developed method. Concentrations in lichen samples were adjusted for recoveries during the data treatment and are summarized in Fig. 2. All results are presented in detail in Tables S4-S7.

Out of the 48 pesticides analyzed, 15 were detected in at least one site. Among them, 13 pesticides are considered priority substances to monitor in the ambient air, and 4 pesticides are currently banned by EU legislation. Fungicides were the most frequently measured, showing a detection rate of 18 %, followed by insecticides (13 %) and herbicides (6 %). Individual pesticide concentrations ranged from 0.5 μg.kg^{-1} to 79.4 μg.kg^{-1}, with the maximum concentration observed for difenoconazole. Lindane, diflufenican, difenoconazole and boscalid were the most ubiquitous pesticides as they were detected in all sites. Despite its ban in 1998 and 2007 for agricultural and biocidal uses, respectively, lindane was found in 100 % of the lichen samples due to its persistence in the environment. This result supported the lindane analyses carried out between 2012 and 2017 in the Provence-Alpes-Côte-d'Azur Region, which showed a detection frequency of 99 % in the ambient air on daily filter samples (Désert et al., 2018). Therefore, it is consistent to find lindane in lichens where the accumulation takes place over several months. Lindane was relatively homogeneously distributed among locations (quantified concentrations ranging from 1.1 to 4.5 μg.kg^{-1}), which is also consistent with a regional-scale distribution, associated with ancient dispersion without recent use. Difenoconazole is a fungicide widely used for disease control in many fruits, vegetables, cereals, and various other grain crops. Its broad range of applications combined

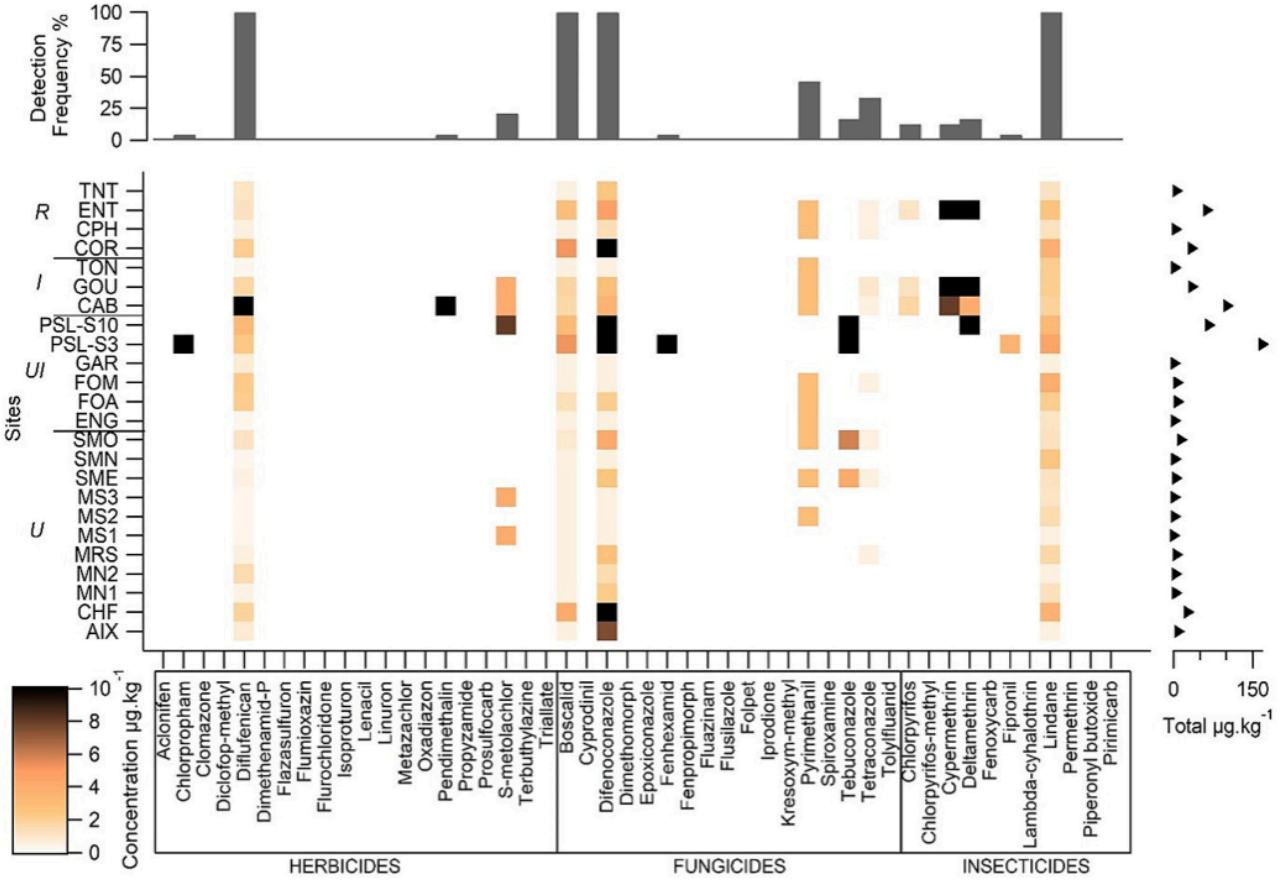


Fig. 2. Abundance of 48 pesticides in lichens sampled on the 24 sites. Each row represents a site and each column, a pesticide. Pesticides are ordered by pesticide class, i.e., herbicides, fungicides, and insecticides. The color range represents the level of the detected concentrations (black cells = concentration > 10 µg.kg^{-1}), whereas empty (white) cells indicate no detection (<LOD). For the pesticides detected but in concentrations under the LOQ, an arbitrary intermediate concentration equal to 2xLOD was assigned. The sum of the concentrations of quantified pesticides (>LOQ) for each site is given on the right. The bars at the top show the frequency of occurrence of each specific compound across all samples.

to its long atmospheric lifetime (Socorro et al., 2016) might explain the high detection rate and concentration levels. Boscalid is an efficient broad-spectrum carboximide fungicide applied to control plant pathogens during the production of numerous crops and fruits, especially in greenhouses. For its part, diflufenican is one of the most used herbicides with multipurpose applications, including urban weed control. Different studies reported the frequent detection of these pesticides in air samples in France and their potential for atmospheric transport which might explain their presence at all the sampling sites (Désert et al., 2018; Mayer et al., 2024; Schummer et al., 2010).

In addition to lindane, three more recently banned pesticides were sporadically detected. It concerns chlorpyrifos, chlorpropham and fipronil. The last two were detected only in one site (PSL—S3, Table S5). This result highlights the fact that the monitoring of banned pesticides should not be overlooked as they can still be employed for domestic uses (i.e. fipronil is allowed for parasite control on pets) or to get rid of old inventory. Significant amounts of the pyrethroids cypermethrin and deltamethrin, the herbicide s-metolachlor and the fungicide tebuconazole were found in several sites whereas the presence of pendimethalin and fenhexamid was clearly identified in one site for each substance. Finally, pyrimethanil and tetraconazole were detected but under the limits of quantification in various sites. All these compounds were also frequently quantified during the study made in this area from 2012 to 2017 (Désert et al., 2018), which confirms a preferential use of these pesticides at the regional scale.

The studies available in the literature that investigated the use of lichens for pesticide monitoring in the atmosphere are scarce and mainly limited to ancient organochlorine pesticides. The average concentrations for lindane and chlorpyrifos reported in the most recent studies ranged from 0.15 µg.kg^{-1} to 10.06 µg.kg^{-1} for lindane and from 1.71 to 2.25 µg.kg^{-1} for chlorpyrifos, levels that are similar to the values found in this work (1.9 µg.kg^{-1} and 1.4 µg.kg^{-1} in average for lindane and chlorpyriphos, respectively) (Table 3). Earlier studies provided historical data on the biomonitoring of lindane in the atmosphere, with concentrations reaching 130 µg.kg^{-1} when the use of lindane was still authorized, and thereafter a decrease was observed over time to get to the current levels (Table 3). Considering that these studies were conducted with different lichen species, in different regions, at different times, and without harmonized sampling and analytical protocols, any interpretation must be made with caution. However, these results still highlight the relevance of lichen biomonitoring for pesticides and the need to extend these measurements to other sites with the development of standardized protocols to facilitate the comparison of results between studies.

3.4. Influence of anthropogenic activities

The total pesticide concentrations exhibited strong differences between locations. Six sites showed higher concentrations compared to the others: PSL-S3 and PSL-S10 (Port-Saint-Louis-du-Rhône), CAB and GOU (Fos-Sur-Mer), ENT (Saint-Martin-de-Crau) and COR (Cornillon-Confoux) with concentrations reaching 168.4 µg.kg^{-1} in total for PSL—S3.

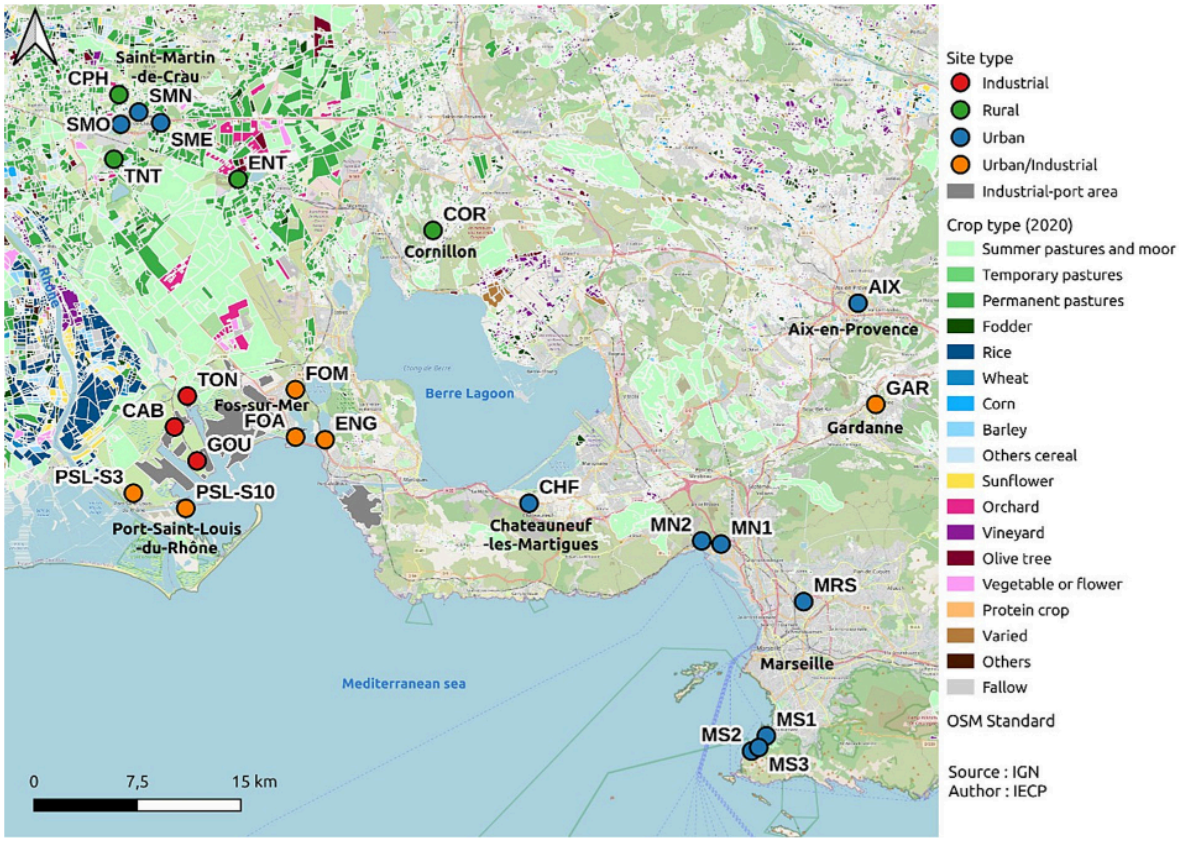


Fig. 3. Crop-type map of the study area. The sampling sites are identified by colored circles according to their typology.

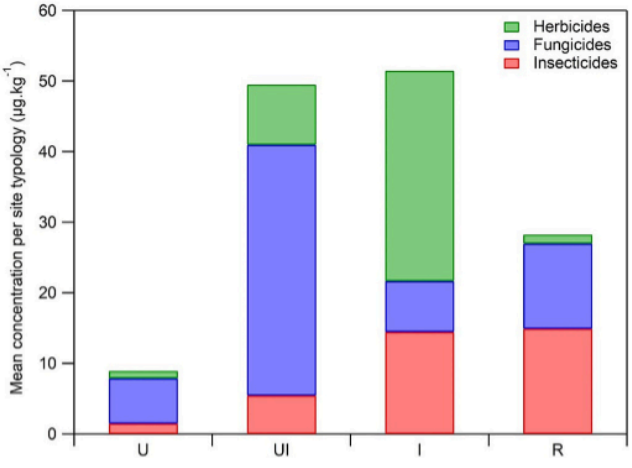


Fig. 4. Distribution of pesticides families i.e. herbicides, fungicides, and insecticides (mean concentrations in lichen) between urban (U), urban/industrial (UI), industrial (I), and rural (R) sites.

Conversely, the lowest total concentrations were found in the South Marseille sites (MS1, MS2, MS3) and Gardanne (GAR) with a total mean concentration of 0.9 µg.kg^{-1}. These high-concentration sites also exhibited the largest number of pesticides detected with 11 and 10 pesticides detected in the CAB and GOU sites respectively. The lichen sampled in the rural site ENT which is located near large orchards, olive trees, and greenhouse vegetable crops (Fig. 3) was characterized by high levels of insecticides (deltamethrin and cypermethrin) widely used in these crop types. Insecticides were also well detected on the west side of the industrial zone, in the sites GOU, PSL—S10, CAB, and PSL—S3, which are all downwind from large agricultural spaces (rice, vineyards, sunflowers, etc.) and possibly impacted by the mosquito control programs in the Camargue and Rhône delta wetlands located on the west side of the study area. Conversely, insecticide levels remained low in urban areas (Fig. 4).

Lichen samples collected in the industrial site CAB, and to a lesser extent, in PSL-S10 and PSL—S3, also had high levels of herbicides. Considering that around industrial installations, roadsides, railway tracks, etc., the aim of herbicides is the absolute destruction of all vegetation that might cause damage, present fire hazards, or impede work crews, these areas may reveal unconsidered hotspots. One such hotspot was identified here in the CAB site, with significantly higher concentrations of diflufenican (64.8 µg.kg^{-1}) and pendimethalin (19.6 µg.kg^{-1}) compared to other sites (not detected to 3.3 µg.kg^{-1}) (Tables S4-S7). Its proximity to a chemical plant and a railway terminal suggests intensive use of herbicides for weed control, including diflufenican, active substance used by the French national railroad company (SNCF). This is particularly concerning as wide-spectrum cocktail effects may arise from numerous chemical contaminants also present in this area (Ratier et al., 2018).

Fungicides were particularly concentrated in the Port-Saint-Louis-du-Rhône samples (PSL-S3 and PSL—S10), with higher concentrations of tebuconazole, difenoconazole, and fenhexamid measured compared to the other sites. The presence of tebuconazole and difenoconazole may result from their use in rice farming which is widely practiced in the Rhône Delta wetlands located northwest of the sampling sites that can consequently be impacted under northwesterly wind conditions (Fig. 3). Additionally, it is worth noting the proximity of cereal and peat terminals with open-air conditioning near these sites which could lead to atmospheric inputs of pesticides from stored cereals and peats. Finally, urban areas showed lower exposure to pesticides in the ambient air

compared to rural and industrial areas, as revealed by integrative lichen biomonitoring, with average concentration levels 3 to 5 times lower than those in rural and industrial sites (Fig. 4).

4. Conclusions

The analytical method presented in this paper enabled the simultaneous analysis of 48 pesticides, mostly currently used or recently banned substances, in the lichen *X. parietina*. The combination of an ASE extraction method with acetonitrile followed by a purification step on an Oasis HLB sorbent allowed an efficient analysis by GC–MS/MS, demonstrated by satisfying recovery rates (ranging from 70 % to 130 %) for 81 % of the targeted pesticides. The validation of the method yielded positive results, indicating good performance in terms of linearity, accuracy, and precision. The analysis of lichen samples collected among 24 sites in various environments enabled the detection of 15 pesticides, including 6 fungicides, 5 insecticides, and 4 herbicides. Lindane, diflufenican, difenoconazole, and boscalid were the most detected at all sites, suggesting possible atmospheric transports at local and regional scales and persistence of these compounds in the atmosphere. The long-term integration achieved with lichen biomonitoring compared to instrumental techniques (filter sampling or on-line measurements) have revealed particularly valuable information concerning the distribution of pesticides according to anthropogenic activities, highlighting poorly documented and unexpected aspects such as the possibly high contamination sources in industrial areas or by transportation infrastructure. A complementary study, including a greater number of sites with similar profiles (crop type, road or rail infrastructures, industrial activity) and a better balance in the number of sites per typology, could be conducted to perform robust statistical analyses, which were not feasible here due to the heterogeneity and specificity of the selected sites. The experimental approach described in this work could be applied to other monitoring campaigns to map the spatial distribution of pesticides useful to identified contaminated areas and aid human health risk assessment studies. The determination of pesticides in lichens also illustrates their uptake by living species, and this monitoring methodology may be extended to other organic contaminants, thus providing information on potential cocktail effects.

CRediT authorship contribution statement

Amandine Durand: Writing – original draft, Visualization, Validation, Methodology, Investigation, Data curation, Conceptualization. **Julien Dron:** Writing – review & editing, Conceptualization. **Pascale Prudent:** Writing – review & editing, Supervision, Project administration, Conceptualization. **Henri Wortham:** Writing – review & editing, Supervision, Conceptualization. **Caroline Dalquier:** Investigation. **Mathilde Reuillard:** Visualization. **Annabelle Austruy:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was financially supported by the French Agency for Ecological Transition (ADEME) within the project EVALVIE (IMPACT 2020 – 22ESD0002-C) and the local authorities, Aix-Marseille-Provence Metropolis and the City of Fos-sur-Mer. The authors are grateful to all the private individuals, communities and public establishments which made their land available for this study.

Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.177286.

Data availability

Data will be made available on request.

References

Abas, A., 2021. A systematic review on biomonitoring using lichen as the biological indicator: a decade of practices, progress and challenges. Ecol. Indic. 121, 107197. https://doi.org/10.1016/j.ecolind.2020.107197.

Augusto, S., Catarino, F., Branquinho, C., 2007. Interpreting the dioxin and furan profiles in the lichen *Ramalina canariensis Steiner* for monitoring air pollution. Sci. Total Envir. 377 (1), 114–123. https://doi.org/10.1016/j.scitotenv.2007.01.089.

Augusto, S., Máguas, C., Matos, J., Pereira, M.J., Soares, A., Branquinho, C., 2009. Spatial modeling of PAHs in lichens for fingerprinting of multisource atmospheric pollution. Environ. Sci. Technol. 43 (20), 7762–7769. https://doi.org/10.1021/es901024w.

Augusto, S., Maguas, C., Matos, J., Maria Joao, M., Pereira, M., Branquinho, C., 2010. Lichen PAH concentrations can identify geographic areas that may be out of compliance with regulatory standards. Environ. Pollut. 158, 483–489.

Augusto, S., Pinho, P., Santos, A., Botelho, M.J., Palma-Oliveira, J., Branquinho, C., 2016. Tracking the spatial fate of PCDD/F emissions from a cement plant by using lichens as environmental biomonitors. Environ. Sci. Technol. 50 (5), 2434–2441. https://doi.org/10.1021/acs.est.5b04873.

Austruy, A., 2022. EVALVIE project: Environmental and health vulnerability assessment of the territories. Rapport d'avancement n°1 - ADEME. Institut Écocitoyen pour la Connaissance des Pollutions.

Bedos, C., Cellier, P., Calvet, R., Barriuso, E., Gabrielle, B., 2002. Mass transfer of pesticides into the atmosphere by volatilization from soils and plants: overview. Agron 22 (1), 21–33. https://doi.org/10.1051/agro:2001003.

Blett, T., Geiser, L., Porter, E., 2003. Air Pollution-Related Lichen Monitoring in National Parks, Forests and Refuges: Guidelines for Studies Intended for Regulatory and Management Purposes. Fish and Wildlife Service and U.S. Forest Service, National Park Service, U.S.

Conti, M., Cecchetti, G., 2001. Biological monitoring: lichens as bioindicators of air pollution assessment — a review. Environ. Pollut. 114 (3), 471–492. https://doi.org/10.1016/s0269-7491(00)00224-4.

Damalas, C.A., Eleftherohorinos, I.G., 2011. Pesticide exposure, safety issues, and risk assessment indicators. Int. J. Environ. Res. Pub. Health. 8 (5), 1402–1419. https://doi.org/10.3390/ijerph8051402.

Dauphin, C.-E., Durand, A., Lubonis, K., Wortham, H., Dron, J., 2020. Quantification of monosaccharide anhydrides by gas chromatography/mass spectrometry in lichen samples. J. Chromatogr. A 1612, 460675. https://doi.org/10.1016/j.chroma.2019.460675.

Désert, M., Ravier, S., Gille, G., Quinapallo, A., Armengaud, A., Pochet, G., Savelli, J.-L., Wortham, H., Quivet, E., 2018. Spatial and temporal distribution of current-use pesticides in ambient air of Provence-Alpes-Côte-d'Azur region and Corsica. France. Atmos. Environ. 192, 241–256. https://doi.org/10.1016/j.atmosenv.2018.08.054.

Dron, J., Ratier, A., Austruy, A., Revenko, G., Chaspoul, F., Wafo, E., 2021. Effects of meteorological conditions and topography on the bioaccumulation of PAHs and metal elements by native lichen (Xanthoria parietina). J. Environ. Sci. 109, 193–205. https://doi.org/10.1016/j.jes.2021.03.045.

Erney, D.R., Gillespie, A.M., Gilvydis, D.M., Poole, C.F., 1993. Explanation of the matrix-induced chromatographic response enhancement of organophosphorus pesticides during open tubular column gas chromatography with splitless or hot on-column injection and flame photometric detection. J. Chromatogr. A 638, 57–63. https://doi.org/10.1016/0021-9673(93)85007-T.

Eurostat, 2024. Pesticide sales in the UE. https://ec.europa.eu/eurostat/databrowser/view/aei_fm_salpest09/default/table?lang=en (last update June 2024).

Fenner, K., Canonica, S., Wackett, L.P., Elsner, M., 2013. Evaluating pesticide degradation in the environment: blind spots and emerging opportunities. Science 341 (6147), 752–758. https://doi.org/10.1126/science.1236281.

Garty, J., 2001. Biomonitoring atmospheric heavy metals with lichens: theory and application. Crit. Rev. Plant Sci. 20 (4), 309–371. https://doi.org/10.1080/20013591099254.

Herzig, R., Lohmann, N., Meier, R., 2019. Temporal change of the accumulation of persistent organic pollutants (POPs) and polycyclic aromatic hydrocarbons (PAHs) in lichens in Switzerland between 1995 and 2014. Environ. Sci. Pollut. Res. Int. 11, 10562–10575. https://doi.org/10.1007/s11356-019-04236-9.

Hulin, M., Leroux, C., Mathieu, A., Gouzy, A., Berthet, A., et al., 2021. Monitoring of pesticides in ambient air: prioritization of substances. Sci. Total Environ. 753, 141722. https://doi.org/10.1016/j.scitotenv.2020.141722.

INSEE, 2021. Institut National de la Statistique et des Etudes Economiques France. https://www.insee.fr/fr/statistiques/ (accessed 10 July 2024).

Inserm, 2022. Effects of pesticides on health: New data. In: Summary. Collection Expertise Collective. EDP Sciences, Montrouge.

Jiménez, J.J., Bernal, J.L., del Nozal, M.J., Toribio, L., Martín, M.T., 1998. Gas chromatography with electron-capture and nitrogen-phosphorus detection in the analysis of pesticides in honey after elution from a Florisil column: influence of the

honey matrix on the quantitative results. J. Chromatogr. A 823, 381–387. https://doi.org/10.1016/S0021-9673(98)00292-1.
Loppi, S., Paoli, L., 2015. Comparison of the trace element content in transplants of the lichen Evernia prunastri and in bulk atmospheric deposition: a case study from a low polluted environment (C Italy). Biologia 70, 460–466. https://doi.org/10.1515/biolog-2015-0053.
Lucadamo, L., Corapi, A., Gallo, L., 2018. Evaluation of glyphosate drift and anthropogenic atmospheric trace elements contamination by means of lichen transplants in a southern Italian agricultural district. Air Qual. Atmos. & Health. 11, 325–339. https://doi.org/10.1007/s11869-018-0547-7.
Mayer, L., Degrendele, C., Šenk, P., Kohoutek, J., Přibylová, P., Kukučka, P., Melymuk, L., Durand, A., Ravier, S., Alastuey, A., Baker, A.R., Baltensperger, U., Baumann-Stanzer, K., Biermann, T., Bohlin-Nizzetto, P., Ceburnis, D., Conil, S., Couret, C., Degórska, A., Lammel, G., 2024. Widespread pesticide distribution in the European atmosphere questions their degradability in air. Environ. Sci. Technol. 58 (7), 3342–3352. https://doi.org/10.1021/acs.est.3c08488.
Météo-France, 2021. https://meteo.data.gouv.fr/datasets/donnees-climatologiques-de-base-quotidiennes/ (accessed 23 April 2024).
Nash, T.H.I.I.I., 2008. Lichen Biology. Cambridge University Press, Cambridge, pp. 1–8.
Nimis, P., Scheidegger, C., Wolseley, P., 2002. Monitoring with Lichens – Monitoring Lichens. Springer, Netherlands.
Nimis, P.L., Andreussi, S., Pittao, E., 2001. The performance of two lichen species as bioaccumulators of trace metals. Sci. Total Environ. 275 (1–3), 43–51. https://doi.org/10.1016/s0048-9697(00)00852-4.
Paoli, L., Vannini, A., Fačkovcová, Z., Guarnieri, M., Bačkor, M., Loppi, S., 2018. One year of transplant: is it enough for lichens to reflect the new atmospheric conditions? Ecol. Indic. 88, 495–502. https://doi.org/10.1016/j.ecolind.2018.01.043.
Parzych, A., Zduńczyk, A., Astel, A., 2016. Epiphytic lichens as bioindicators of air pollution by heavy metals in an urban area (northern Poland). J. Elem. 21 (3), 781–795. https://doi.org/10.5601/jelem.2016.21.1.861.
Pimentel, D., Burgess, M., 2012. Small amounts of pesticides reaching target insects. Environ. Dev. Sustain. 14, 1–2. https://doi.org/10.1007/s10668-011-9325-5.
Poole, C.F., 2007. Matrix-induced response enhancement in pesticide residue analysis by gas chromatography. J. of Chromatogr. A. 1158 (1–2), 241–250. https://doi.org/10.1016/j.chroma.2007.01.018.
Ratier, A., Dron, J., Revenko, G., Austruy, A., Dauphin, C.E., Chaspoul, F., Wafo, E., 2018. Characterization of atmospheric emission sources in lichen from metal and organic contaminant patterns. Environ. Sci. Pollut. Res. 25, 8364–8376. https://doi.org/10.1007/s11356-017-1173-x.
Sánchez-Brunete, C., Albero, B., Martín, G., Tadeo, J.L., 2005. Determination of pesticide residues by GC-MS using Analyte protectants to counteract the matrix effect. Anal. Sci. 21, 1291–1296. https://doi.org/10.2116/analsci.21.1291.
Schrlau, J.E., Geiser, L., Hageman, K.J., Landers, D.H., Simonich, S.M., 2011. Comparison of lichen, conifer needles, passive air sampling devices, and snowpack as passive sampling media to measure semi-volatile organic compounds in remote atmospheres. Environ. Sci. Technol. 45 (24), 10354–10361. https://doi.org/10.1021/es202418f.
Schummer, C., Mothiron, E., Appenzeller, B.M.R., Rizet, A.L., Wennig, R., Millet, M., 2010. Temporal variations of concentrations of currently used pesticides in the atmosphere of Strasbourg. France. Environ. Pollut. 158 (2), 576–584. https://doi.org/10.1016/j.envpol.2009.08.019.
Socorro, J., Durand, A., Temime-Roussel, B., Gligorovski, S., Wortham, H., Quivet, E., 2016. The persistence of pesticides in atmospheric particulate phase: an emerging air quality issue. Sci. Rep. 6, 33456. https://doi.org/10.1038/srep33456.
Studabaker, W.B., Puckett, K.J., Percy, K.E., Landis, M.S., 2017. Determination of polycyclic aromatic hydrocarbons, dibenzothiophene, and alkylated homologs in the lichen *Hypogymnia physodes* by gas chromatography using single quadrupole mass spectrometry and time-of-flight mass spectrometry. J. Chromatogr. A 1492, 106–116. https://doi.org/10.1016/j.chroma.2017.02.051.
Tudi, M., Ruan, H.D., Wang, L., Lyu, J., Sadler, R., Connell, D., Chu, C., Phung, D.T., 2021. Agriculture development, pesticide application and its impact on the environment. Int. J. Environ. Res. Pub. Health. 18 (3), 1112. https://doi.org/10.3390/ijerph18031112.
Van der Wat, L., Forbes, P.B.C., 2019. Comparison of extraction techniques for polycyclic aromatic hydrocarbons from lichen biomonitors. Environ. Sci. Pollut. Res. 26, 11179–11190. https://doi.org/10.1007/s11356-019-04587-3.
Vannini, A., Guarnieri, M., Paoli, L., Sorbo, S., Basile, A., Loppi, S., 2016. Bioaccumulation, physiological and ultrastructural effects of glyphosate in the lichen *Xanthoria parietina* (L.) Th. Fr. Chemosphere 164, 233–240. https://doi.org/10.1016/j.chemosphere.2016.08.058.
Villeneuve, J.P., Fogelqvist, E., Cattini, C., 1988. Lichens as bioindicators for atmospheric pollution by chlorinated hydrocarbons. Chemosphere 17 (2), 399–403. https://doi.org/10.1016/0045-6535(88)90230-5.
Yusà, V., Coscollà, C., Mellouki, W., Pastor, A., de la Guardia, M., 2009. Sampling and analysis of pesticides in ambient air. J. Chromatogr. A 1216, 2972–2983. https://doi.org/10.1016/j.chroma.2009.02.019.
Zhao, L., Zhang, C., Jia, S., Liu, Q., Chen, Q., Li, X., Liu, X., Wu, Q., Zhao, L., Liu, H., 2019. Element bioaccumulation in lichens transplanted along two roads: the source and integration time of elements. Ecol. Indic. 99, 101–107. https://doi.org/10.1016/j.ecolind.2018.12.020.
Zhu, N., Schramm, K.W., Wang, T., Henkelmann, B., Fu, J., Gao, Y., Wang, Y., Jiang, G., 2015. Lichen, moss and soil in resolving the occurrence of semi-volatile organic compounds on the southeastern Tibetan plateau. China. Sci. Total Environ. 518–519, 328–336. https://doi.org/10.1016/j.scitotenv.2015.03.024.
Zivan, O., Bohbot-Raviv, Y., Dubowski, Y., 2017. Primary and secondary pesticide drift profiles from a peach orchard. Chemosphere 177, 303–310. https://doi.org/10.1016/j.chemosphere.