Pesticides in roof runoff: Study of a rural site and a suburban site

C. Vialle[a,b,*], C. Sablayrolles[a,b], J. Silvestre[c,d], L. Monier[e], S. Jacob[e], M.-C. Huau[f], M. Montrejaud-Vignoles[a,b]

[a] Université de Toulouse, INP, LCA (Laboratoire de Chimie Agro-Industrielle), ENSIACET, 4 Allées Emile Monso, F-31030 Toulouse, France
[b] INRA, LCA (Laboratoire de Chimie Agro-Industrielle), F-31029 Toulouse, France
[c] Université de Toulouse, INP, ENSAT, Avenue de l'Agrobiopole, F-31326 Castanet-Tolosan, France
[d] UMR 5245 CNRS/INP/UPS, EcoLab (Laboratoire d'écologie fonctionnelle), 29 Rue Jeanne Marvig, F-31055 Toulouse Cedex, France
[e] Veolia Eau, Direction Technique, Immeuble Giovanni Battista B, 1 Rue Giovanni Battista Pirelli, F-94410 Saint-Maurice, France
[f] Veolia Eau, 36-38 Avenue Kleber, F-75016 Paris, France

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ABSTRACT

The quality of stored roof runoff in terms of pesticide pollution was assessed over a one year period. Two tanks, located at a rural and suburban site, respectively, were sampled monthly. The two studied collection surface were respectively a tile slope roof and a bituminous flat roof. Four hundred and five compounds and metabolites were screened using liquid and gas chromatography coupled with various detection systems. Principal Component Analysis was applied to the data sets to elucidate patterns. At the rural site, two groups of compounds associated with two different types of agriculture, vineyard and crops, were distinguished. The most frequently detected compound was glyphosate (83%) which is the most commonly used herbicide in French vineyards. At the suburban site, quantified compounds were linked to agriculture rather than urban practices. In addition, all samples were contaminated with mecoprop which is a roof protecting agent. Its presence was attributed to the nature of roofing material used for rainwater collection. For both sites, the highest number and concentrations of compounds and metabolites were recorded at the end of spring and through summer. These results are consistent with treatment periods and higher temperatures.

1. Introduction

Pesticides are dangerous environmental pollutants because of their toxicity and long lifetime in the environment. The main route by which pesticides enter the atmosphere is evaporation during their application or evaporation from soil or plant surfaces after application (Spencer and Cliath, 1990). The application of pesticides can be linked to agricultural and non agricultural uses. Atmospheric removal occurs by dry or wet deposition. Pesticides deposited from the atmosphere can come from local sources but also from long range atmospheric transport (Bildeman et al., 1993; Zabik and Seiber, 1993).

Precipitation thus is likely to be contaminated by pesticides. Previous studies have determined the abundance of widely used pesticides in rainwater; some were reviewed by Dubus et al. (2000). More recent studies have investigated the link between toxicity of rainwater and the presence of pesticides (Hamers et al., 2001, 2003; Rouvalis et al., 2009) as well as the seasonal and spatial fluctuations of pesticide contamination (Hamers et al., 2003).

Fewer studies have examined the quality of roof runoff with respect to pesticide concentrations. Investigations were performed in Switzerland (Bucheli et al., 1998a), and in the urban region of Gdansk in Poland (Polkowska et al., 2002, 2009; Tsakovski et al., 2010). Roof runoff can be considered a nonpoint pollution source (Chang et al., 2004). Pollutants deposited on the roof surface during the dry period are washed out by the precipitation at a later date. In addition, some roofing materials also contribute to pesticide pollution if they have been treated to prevent plant growth (Bucheli et al., 1998b).

The study of pesticide concentrations in roof runoff is all the more important as roof runoff is being collected for reuse: collected rainwater can be used as a substitute for valuable drinking water, a practice that is more and more common. In France, only external uses of roof runoff (e.g., garden watering, cleaning) were formerly allowed, except in special cases (drought, no mains network).

* Corresponding author. ENSIACET, LCA, 4 Allées Emile Monso, BP 44362, F-31030 Toulouse, France. Tel.: +335 34 32 35 51; fax: +335 34 32 35 97.
E-mail address: claire.vialle@ensiacet.fr (C. Vialle).

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Nevertheless, rainwater harvesting devices are already available in the market; according to suppliers, 10 000 systems were in use in 2007, out of which 67 were used in large buildings. The increasing demand from private customers has leveraged reconsidering rainwater harvesting, and a new decree authorised and clarified rainwater use inside buildings in August 2008 (Decree of August 21st, 2008). Even though there were investigations of rainwater reuse development at a large scale, French law still forbids the use of rainwater for drinking.

Principal Component Analysis is one of the most applied approaches in environmetrics to study data structures. It is aimed at finding and interpreting hidden complex and casually determined relationships between dataset features. This is accomplished by studying the data structure in a reduced dimension while retaining the maximum amount of variability present in the data. To do this, it is necessary to estimate the number of significant components present in the data. More precisely, a matrix of pairwise correlations among parameters is decomposed into eigenvectors, which in turn are sorted in descending order of their corresponding eigenvalues. At this point, raw data are generally unsuitable for statistical analyses because of differences in the sizes of the variables. Mathematically, PCA normally involves three major steps: 1) the standardisation of measurements to ensure that they have equal weights in the analysis by autoscaling the data to produce new variables, thus the mean is equal to zero and the standard deviation is equal to the unit; 2) calculation of the covariance matrix by identifying the eigenvalues and their corresponding eigenvectors; and 3) the elimination of components that account only for a small proportion of the variation in data sets.

This study reports measured pesticide concentrations in roof runoff waters from both a rural area and an urban agglomeration. Generally, compounds were chosen for analysis because they are on the priority list of the European Union. In this study, more than 400 compounds and metabolites were screened. In addition, an effort was made to elucidate patterns in the dataset using Principal Component Analysis.

2. Material and methods

2.1. Sampling site

Two sites in south western France were selected to install commercially available domestic rainwater collection systems (Sotralentz Habitat) which characteristics are detailed in Table 1.

Rainwater is first collected from the roof area and then channelled via gutters through pipes to an underground PEHD storage tank in order to be reused later. Prior to entering the tank, the water is passed through a screen rake.

The first site was a private house surrounded by cultivated fields (See Supplementary Material 1 (SM1). This site was located near a rural village 40 km north west of Toulouse. The annual average rainfall in this region is 760 mm, and the average temperatures range from 7.9 to 18.3 °C. Agriculture in this area is characterised by the vineyards of Gaillac and crops such as wheat, maize and colza.

The second site was the research building of an engineering school located in the suburban area of Toulouse, which has an urban population of around 860 000 inhabitants. This site is 12 km from the city centre. The annual average rainfall is 668 mm, with average temperature ranging from 8.6 °C to 18.1 °C. The area is near a well travelled road and 70 ha of experimental cultivation fields (See SM1). The corresponding rotation crop and wind direction are presented on Fig. 1.

Table 1
Characteristics of the two sampling sites.

	Location	Roof type	Roof area (m^2)	Tank volume (m^3)
Site 1	Rural	Tiles Sloping roof	204	5
Site 2	Suburban	Bituminous Flat roof	1650	30

2.2. Sample collection

Stored roof runoff sampling was carried out monthly from January 2009 to December 2009 for site 1 and between November 2009 and October 2010 for site 2. The sampling was performed using a sampling rod and a beaker. Prior to sampling, the beaker was disinfected with ethanol, rinsed once with ultra high quality water and then rinsed twice with tank water. Grab samples of stored roof runoff were taken around 10 cm under the surface water in the tank. Samples were stored in polyethylene bottles and frozen until analysis.

2.3. Pesticide analysis

Analysis was performed by La Drôme Laboratoires.[1] Water samples were screened for 405 compounds (See SM2). Liquid–liquid extractions with a dichloromethane/ethyl acetate mix (80/20, v:v) at various pH levels were conducted for each sample. Extracts were simultaneously analysed by liquid chromatography (HPLC) and gas chromatography (GC) with systematic multidetection: with diode array detector (HPLC–DAD), coupled with tandem mass spectrometry (HPLC–MS–MS), with an electron capture detector and a nitrogen phosphorus detector (GC–ECD–NPD), or coupled with mass spectrometry (GC–MS). Other sample aliquots were analysed by HPLC after a derivation, or by headspace with GC–MS. Some compounds were quantified by direct injection and analysis by HPLC–MS–MS.

2.4. Principal Component Analysis

In this study, PCA was performed using the commercial software XL stat.

A data matrix, with columns representing the different samplings (12 observations per site) and rows corresponding to the measured compounds (variables), was constructed for analysis with PCA. For standardization each variable was replaced by its value minus the average of the variable and dividing by the standard deviation of the variable.

Values less than the quantification limit were considered to be half of the quantification limit, and values less than the detection limit were considered to be zero. Pearson's correlations between different compounds were first obtained. Then components were determined, and the two first components (F1 and F2) corresponding to the greatest part of the total variance of the data set were retained.

3. Results and discussion

Loadings for the two first components and square cosines are presented in a circle (Figs. 2 and 3a). A variable is increasingly well represented by a component as the corresponding square cosine

[1] La Drôme Laboratoires, 37 avenue de Lautagne, BP 118, 26904 Valence cedex 9, France.

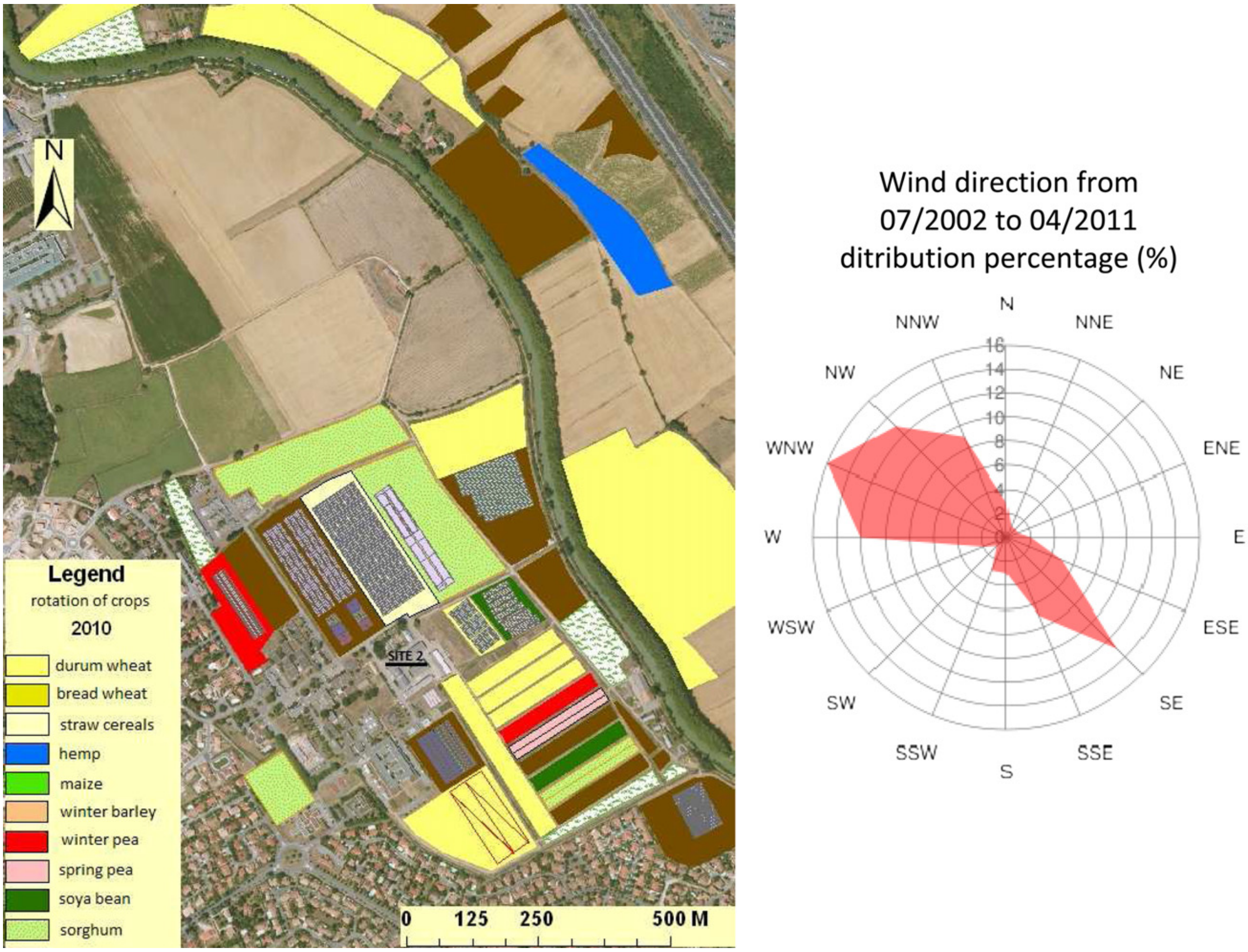

Fig. 1. Crops rotation and wind direction at the suburban site.

nears unity. Graphically, this is represented as the variable nearing the edge of the circle. To elucidate the seasonal influence on concentrations of compounds, different observations were also represented in planes F1 versus F2 (Figs. 2 and 3b).

3.1. *Rural site*

At the rural site, the most frequently detected compounds were glyphosate (83%), DNOC (75%), AMPA (58%), metolachlor (R + S) (58%), carbendazim (50%), and 2,4 MCPA (50%). Analysis revealed that the highest concentrations measured were for glyphosate (6 $\mu g\ L^{-1}$). In addition, concentrations of several hundreds of ng L^{-1} were measured for AMPA, metolachlor, DNOC and metaldehyde in order of decreasing concentrations (See SM3). As a reference, limit values in potable water are 0.1 $\mu g\ L^{-1}$ per pesticide and 0.5 $\mu g\ L^{-1}$ for the sum, according to French regulation. Quantitative fluctuations of these compounds during the year are represented in Fig. 4. Types of compounds detected are consistent with the agricultural practices in the region. In rural zones, herbicides are predominantly used, with fungicides being the next most common. Insecticides are used only to a minor extent.

Strong correlations against the occurrence of some compounds were revealed by the observation of the Pearson's correlation table. Thus, two groups of compounds were distinguishable Fig. 2a. For the first one, the concomitant presence of certain compounds in the rural area can be attributed to the proximity with a vineyard. For example, glyphosate is the most commonly used herbicide in French vineyards. Dimethomorph and iprovalicarb are used to fight mildew, tebuconazole is used against powdery mildew, and boscalid is employed against botrytis. It must be highlighted that folpel, considered as an herbicide and used by vineyards in the region, was not quantified in this study. Compounds composing the second group were more characteristic of pesticides used on crops. Acetochlor is an herbicide principally used on maize in the early growth stages. Pendimethaline is used on sunflower, wheat and maize crops. Metolachlor is also used on maize, whereas aclonifen is often used on sunflower crops. Carbendazim is a pesticide mostly used for market gardening. No comment can be given for the third group, as it is not well represented compared to the two first components. Nevertheless, chlormequat chlorure, isoproturon and chlortoluron are all compounds primarily used on winter crops.

The presence of compounds at the end of spring and in the summer is illustrated in Fig. 2b. Some summer samples are well represented in the first group, corresponding to vineyard pesticides, and the spring sampling is well represented in the second group, corresponding to crop pesticides. Other samples, mainly those collected in autumn and winter, are located in the area described by the third group, representing winter crops. As a result, the distinction of samples of the same season is obviously due to agricultural uses. The ambient temperature may also have an influenced.

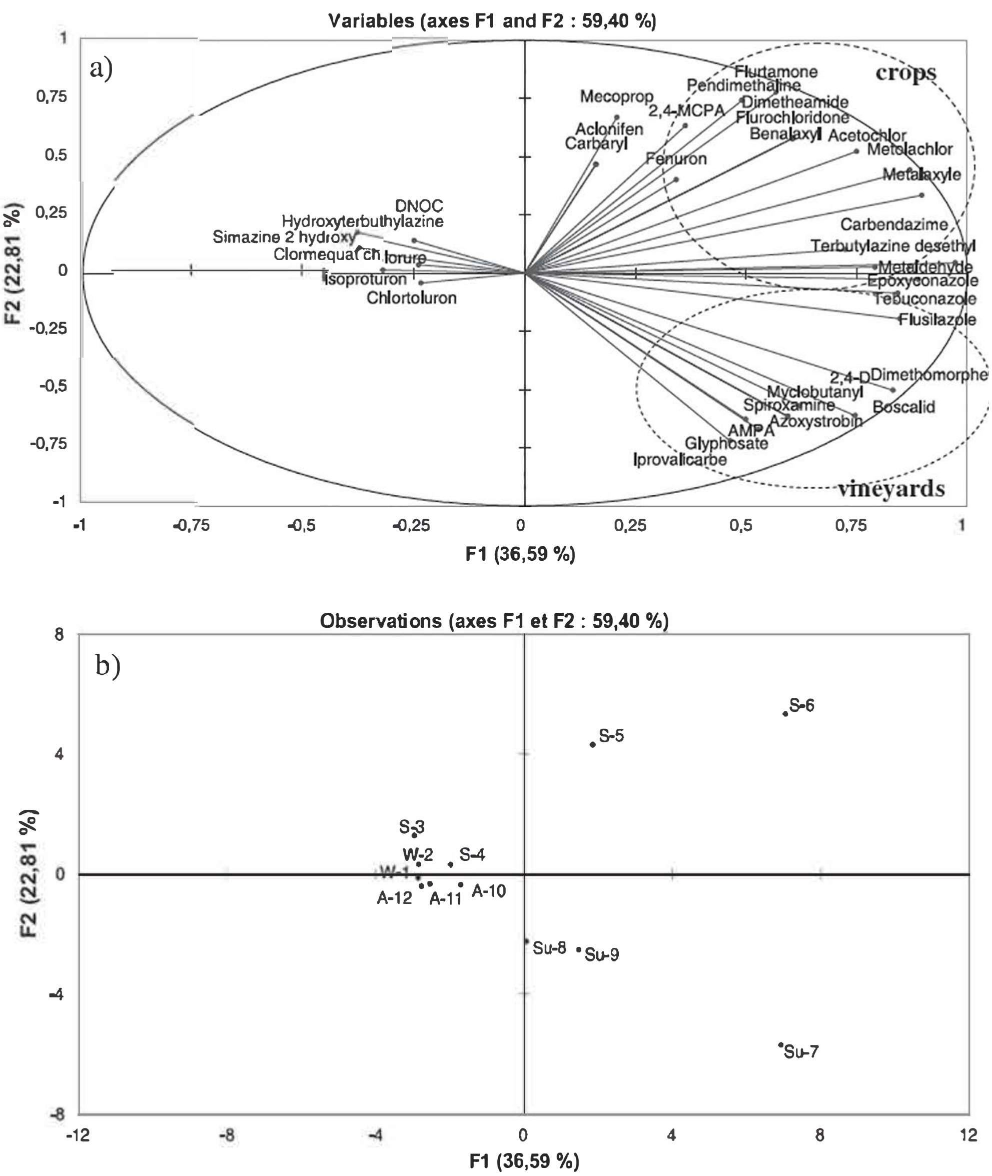

Fig. 2. a) The square cosines for all detected pesticides at site 1 (rural) in components F1 and F2 account for approximately 59% of the total variance. b) A two-dimensional plot of the 12 observations at site 1 (rural) in F1 and F2. The letters indicate the sampling season and the number precises the sampling month (Su Summer; A Autumn, W Winter, S Spring; 1 November; 2 December; 3 January…12 October).

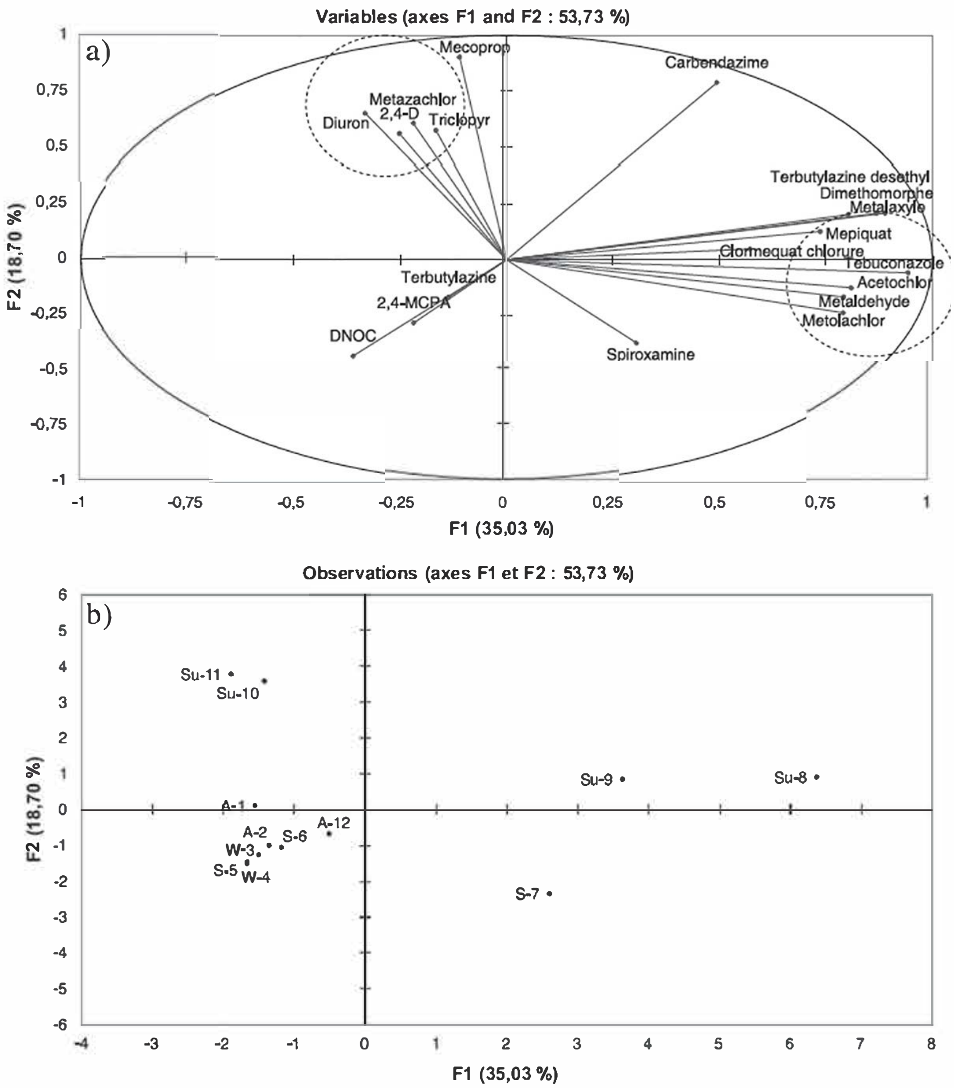

Fig. 3. a) The square cosines for all detected pesticides at site 2 (suburban) in components F1 and F2 account for approximately 55% of the total variance. b) A two-dimensional plot of the 12 observations at the suburban site in F1 and F2. The letters indicate the sampling season and the number precises the sampling month (Su Summer; A Autumn, W Winter, S Spring; 1 January; 2 February; ...11 November; 12 December).

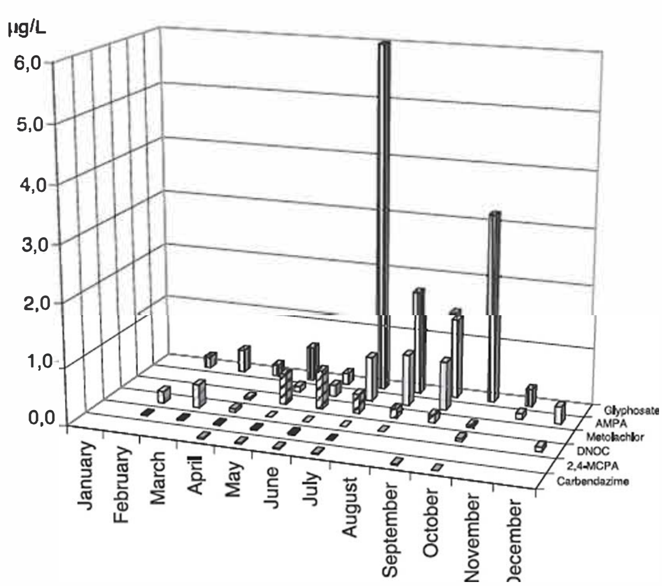

Fig. 4. Concentrations over the year for pesticides detected frequently at the rural site.

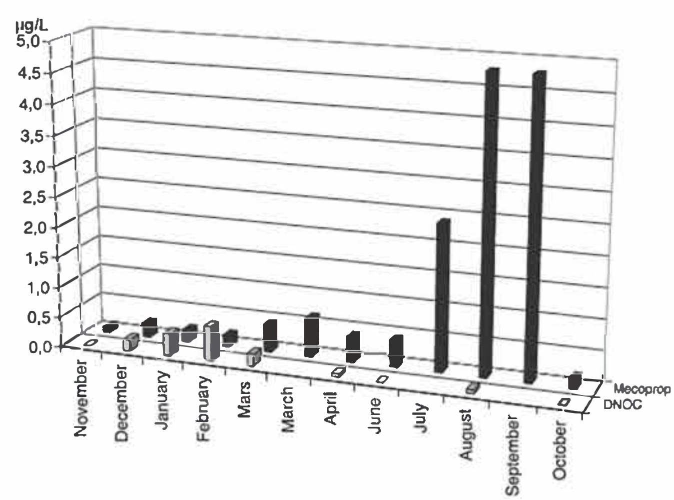

Fig. 5. Concentrations over the year for the pesticides detected frequently at the suburban site.

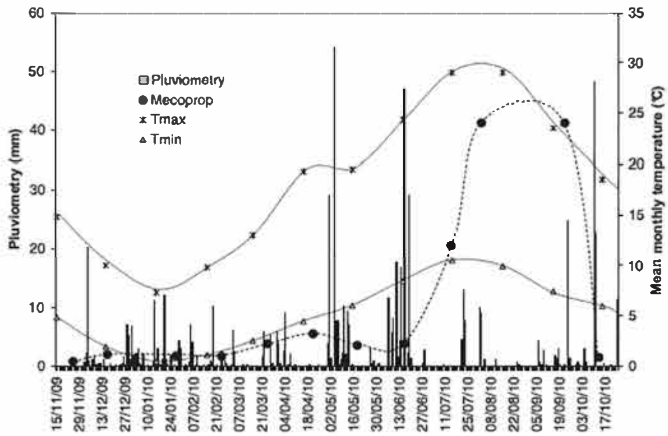

Fig. 6. Evolution of the concentration of mecoprop in roof runoff at the suburban site over the sampling year: influence of ambient temperature.

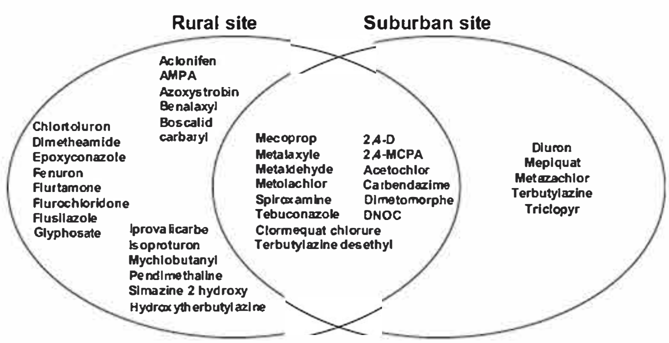

Fig. 7. Pesticides detected according to sampling site.

3.2. Suburban site

At the suburban site, the most often detected compounds, which appeared in at least 50% of the suburban samples, were mecoprop (100%) and DNOC (75%). The compound with the highest measured concentrations was mecoprop (4.8 μg L^{-1}). Up to hundreds of ng L^{-1} were quantified for DNOC, metaldehyde, 2,4 MCPA, and metolachlor (See SM4). Concentration variations during the year for these compounds are represented in Fig. 5.

The percentage of occurrence of mecoprop in roof runoff at the suburban site was 100%. Mecoprop is a roof protecting agent. Thus, in this study, this compound comes from the roofing material itself. The release appeared predominantly when the ambient tempera ture was high. Thus, the maximum concentration was observed in the summer (Fig. 6). This observation is in agreement with obser vations reported by Bucheli et al. (1998b).

Principal Component Analysis resulted in the distinction of two principal groups of compounds (Fig. 3a). Sets of compounds were composed not only of the herbicides or fungicides already quanti fied in the rural area and commonly used in agriculture but also of pesticides used on fruit trees. As in the rural zone, the represen tation of samplings on the two first principal components is used to highlight the particularity of the compounds concentrations during the end of spring and summer (Fig. 3b). The suburban site studied seems to be influenced by nearby agriculture pesticide use rather than urban pesticide practices.

3.3. Comparison of the two sites

Of the 405 pesticides and metabolites analysed, 34 were detected more than once in the roof runoff samples collected at the rural site, of which 26 were above the limit of quantification at least once. At the suburban site, 15 pesticides were quantified, and only 4 were detected more than once over the twelve samples. The ma jority of compounds found were herbicides; the next most common compounds found were fungicides. Metabolites were the third most common class of compounds found.

Concerning the spatial variation, compounds detected in the tanks are different for the two sites. There were 14 compounds detected at least once at both of the two sites; 20 compounds were found only in the rural zone, and 5 were detected exclusively in the suburban area (Fig. 7).

Considering only the number of compounds detected, a greater diversity of compounds was observed in the rural zone. Concerning

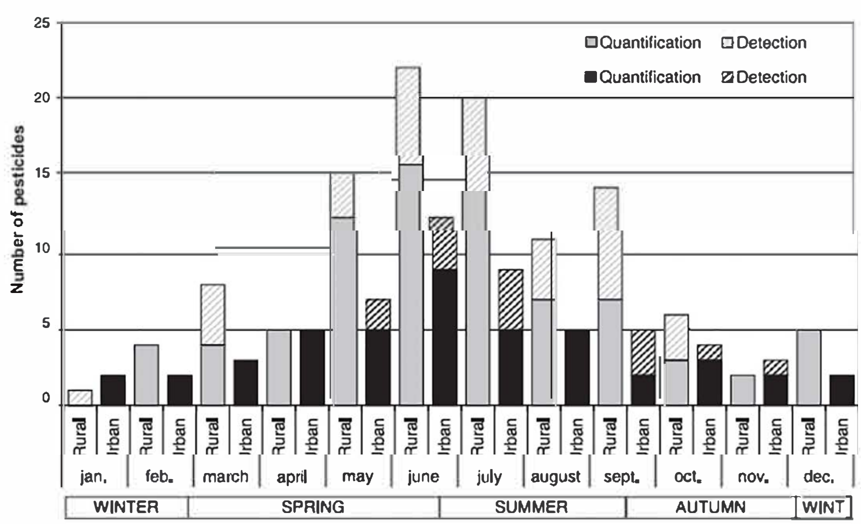

Fig. 8. Number of pesticides detected or quantified over the year at the two sites.

the seasonal variation of the number of compounds detected, conclusions are identical for the two study sites. The most complex mixtures of compounds were sampled at the end of spring through summer at both sites (Fig. 8).

4. Conclusions

This study presents results concerning the quality of stored roof runoff in terms of pesticide contamination. No less than 405 com pounds or metabolites were screened over a year for both a rural and a suburban site in south west France. Even if this study is based on a limited data set, an effort was made to extract more infor mation from the data set through the use of multivariate analysis techniques. At the rural site, PCA permits distinguishing com pounds according to the type of surrounding agriculture, i.e., vineyard and crops. At the suburban site, the presence of com pounds seems to be influenced more by local agriculture than by urban practices. Both sites at the end of spring through the summer were identified as particularly sensible seasons for compounds concentration and diversity. High concentrations of a roof protecting agent were quantified in roof runoff from a bitumi nous flat roof. In the context of rainwater harvesting, which is becoming a common practice, this study reveals the importance of collected roof runoff pollution in terms of pesticides concentra tions. Not only seasonal but also spatial variability of this contam ination over the year was monitored.

Appendix A. Supplementary data

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.jenvman.2013.02.023.

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