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Survey of pesticide residues in Swiss and foreign Wines

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Introduction

The protection of human health from exposure to pesticide residues in foodstuffs remains a major objective. To control the principal parasites of vineyards (moulds, insects or weeds), insecticides and fungicides have to be used, and at harvest time one can find pesticide residues on grapes. Some of these residues pass into the processed products depending on the technological process. Several studies about the fate of pesticide residues from grapes to wine were done and a review was published recently (1). Some substances such as penconazole, fluazinam, kresoxim-methyl and organophosphorous insecticides disappeared quickly from the grapes after treatments, whereas numerous pesticides have longer decay times ($t_{1/2}$ ranged between 10–30 days, 57 days for pyrimethanil) and are still present at harvest time. The pesticides behaviour during the wine making process was also studied. Usually, after fermentation with or without skins, pesticide residue levels in wine decrease compared to those on the grapes and in must, except for some pesticides which have no preferential partition between the liquid (must) and solid (lees and cake) phases such as azoxystrobin or pyrimethanil. For these substances, the concentrations measured in wines were almost the same as on the grapes. Among the clarifying substances (bentonite, charcoal, gelatine, polyvinylpolypyrrolidone, potassium caseinate and colloidal silicon dioxide), only charcoal guaranteed total removal of residues for most pesticides (1). Therefore, if grapes contain high levels of some kind of pesticides, the latter can survive to the wine-making process and contaminate the final product.

To ensure the food safety for consumers, numerous legislations such as the EU directives (2) or the Swiss regulations (3) as well as the Codex alimentarius of FAO/WHO have established maximum residue limits (MRL) for pesticides in foodstuffs and in wine.

Several surveys for controlling pesticide residues in wine have been published, generally based on gas chromatography (GC) monitoring with electron capture detection (ECD), nitrogen-phosphorus detection (NPD) or mass spectrometric (MS) detection (4–9). However, many pesticides, which are thermally unstable or non-volatile such as carbamates, benzimidazoles or triazoles, are difficult or impossible to analyze using GC techniques. Moreover, these substances are generally more soluble in water and the probability of finding them in wine is high. Liquid chromatography (LC) coupled with tandem mass spectrometry (MS/MS) offers a powerful alternative tool for the determination of these compounds in food samples (10–12). A LC-MS/MS method with a simplified extraction procedure was developed as a complement to traditional GC pesticide determination in order to make an effective control of pesticide residues in fruits and vegetables (13, 14), and is now applied to wines.

This paper presents the results obtained from the survey of local wine production in comparison with imported products. Around 250 wines were sampled directly from Geneva area wine-growers and in sales fronts. Organic wines were also studied, in order to control the compliance with the organic reglementation (15) and to observe the level of the environmental pesticide contamination.

Experimental

Sampling

246 samples were taken directly from Geneva area wine growers and from the market in Geneva area: 132 Swiss wines, of which 98 from Geneva producers, and 114 from importation. Foreign wines were from France (19 samples), Italy (18), Spain (14), Australia (6), Argentina and Chile (21), USA (10), South Africa (4) and others countries (4), representing all major wine producing countries. Among these samples, 148 were red wines, 86 white wines, 7 Rosé wines and 2 sparkling wines. The white wine varieties were principally chasselas, chardonnay, white pinot, grey pinot, aligoté and sauvignon. The red wine varieties were principally gamay, red pinot, carbernet-sauvignon, shiraz, merlot and numerous samples were a blending of wine varieties. The years of the wine productions were from 2000 to 2003.

Analytical Methods

In order to screen a very large number of pesticides, we used two different multiresidue methods. The overall schematic procedure is shown in figure 1.

Apolar pesticides such as organochlorine and organophosphorous fungicides and insecticides, are extracted with acetonitrile. After addition of water, pesticides are extracted by liquid-liquid extraction with hexane. The hexane portion is collected and analyzed by gas chromatography (GC) on analytical capillary columns of different polarities (DB-5 and SPB-20) with electron capture (ECD) and nitrogen-phosphorus (NPD) detection. In case of ambiguous identification or for not compliant samples, confirmations are carried out with mass spectrometric (MS) detection. Polar pesticides such as carbamates, benzimidazoles and triazoles, are

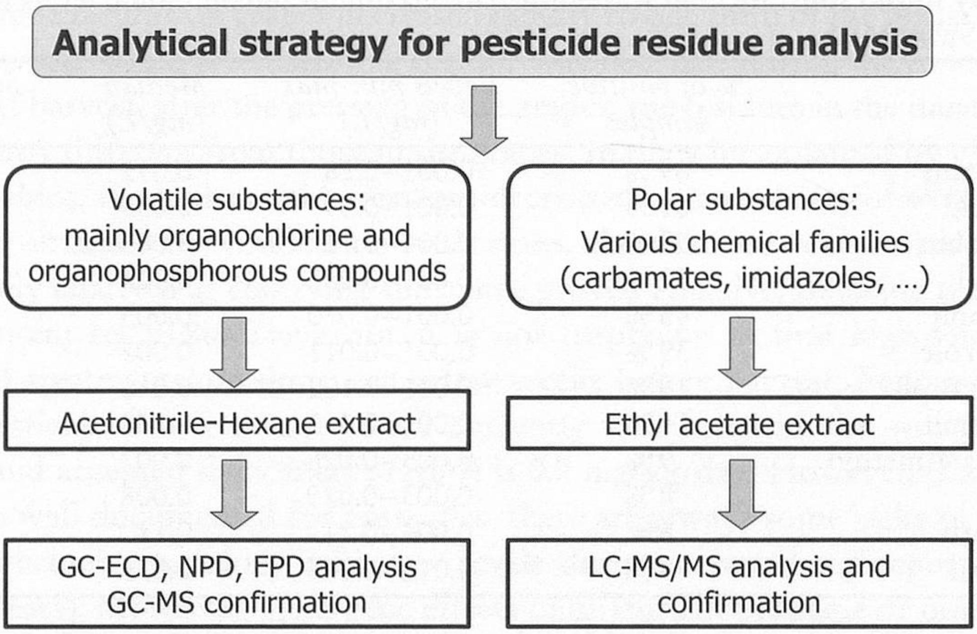

Figure 1 **Overall scheme of the analytical strategy for the pesticide residue survey**

extracted from samples with ethyl acetate. Except for a concentration step, no additional clean-up is necessary. Analyses are performed by liquid chromatography coupled to electrospray ionization and tandem mass spectrometry (LC-ESI-MS/MS) (13). This multiresidue method was up-graded and now allows the determination of 140 pesticides commonly used in crop protection.

Results and discussion

Conventional culture

We analysed 176 wines from conventional culture and found residues in 95 % of the samples indicating that pesticide treatments are really often used. Around 25 active substances used as fungicides or insecticides were detected. The most frequently used pesticides are given in table 1, with indication of the minimum, maximum and median residue levels and the corresponding Swiss MRLs. For example, the fungicide fenhexamid was present in 61 % of the samples with a maximum concentration of 0.59 mg/L and a Swiss MRL of 1.5 mg/L. The following pesticides were found in less than 5 % of the samples: spiroxamine, procymidone, diethofencarb, benodanil, chlorothalonil, cyproconazole, tebufenozide, metalaxyl, spinosad, dimethoate, fuberidazole, oxadixyl, pyrifenox and thiabendazol.

The total pesticide residues measured ranged between 1 and 700 µg/L. All samples complied with the legal requirements and none exceeded the MRL. This demonstrates that treatments were done correctly and that dose, number of applications and withdrawal times before harvest were respected.

Table 1
Frequently found substances in wines. Median, maximum and minimum levels with corresponding Swiss MRL

Pesticide	*% of positive samples*	*Levels min-max (mg/L)*	*Median (mg/L)*	*Swiss MRL (mg/L)*
Carbendazim	69%	0.001–0.28	0.012	2
Fenhexamid	61%	0.001–0.59	0.035	1.5
Azoxystrobin	59%	0.001–0.11	0.005	0.5
Cyprodinil	52%	0.001–0.083	0.008	0.5
Pyrimethanil	45%	0.001–0.070	0.005	1
Tebuconazole	39%	0.001–0.011	0.002	0.3
Dimethomorph	19%	0.001–0.102	0.010	0.2
Myclobutanil	14%	0.001–0.013	0.002	–
Thiophanate-methyl	9%	0.003–0.026	0.007	2
Carbaryl	8%	0.003–0.079	0.008	3
Iprovalicarb	6%	0.004–0.21	0.11	1
Fludioxonil	3%	0.016–0.066	0.035	0.5

Overall results for each wine origin are presented in figure 2. We observed that Swiss wines are generally more contaminated than foreign wines. This can be explained by the fact that the climate of our country is more favourable to fungic diseases than the climate of Southern countries. In fact, concerning the high level of pesticide residue in Swiss wines is mainly caused by one fungicide, fenhexamide. Nowadays, fenhexamide is one of the fungicides mostly used in vineyards protec-

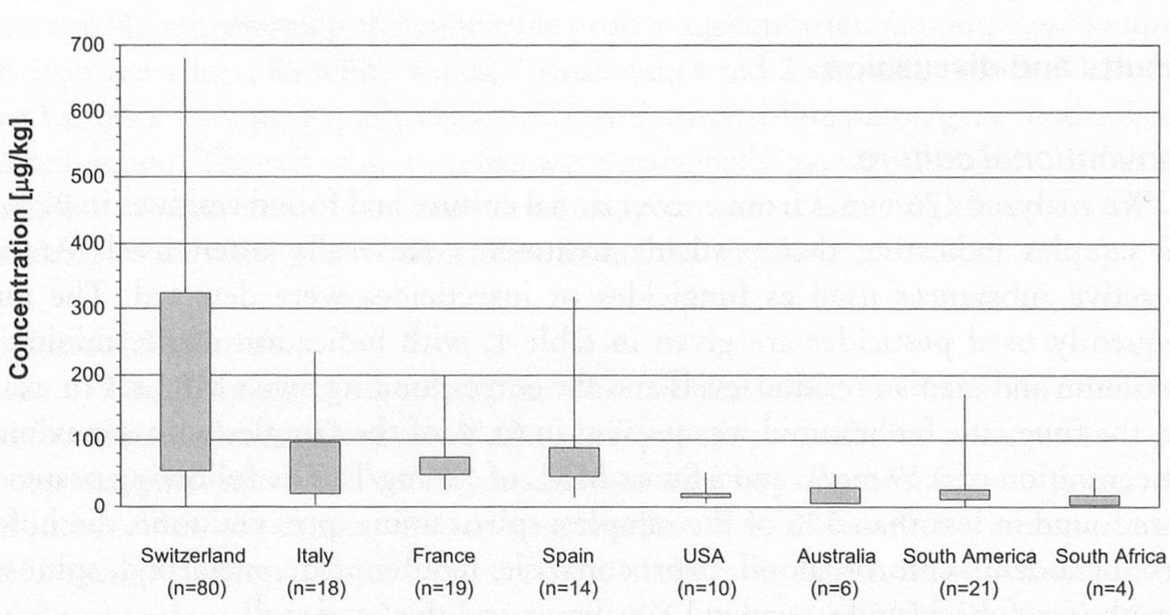

Figure 2 **Total pesticide residue concentrations measured in conventional wines for each origin.**
Rectangles represent 50% of samples and the line indicates the minimum and maximum observed concentrations

tion and its fate from grapes to wine has also been studied (16). After treatment, fenhexamide residue on grapes decreased rapidly to one third of the initial level after the first week, while the remaining residue was constant during the following two weeks. At harvest, after the pressing of the grapes, the residues in the must were not significantly different from those in the grapes. In the wine obtained by vinification without skins, the fenhexamide residues decreased on an average of 49 %, while in the wine obtained by vinification with skins, the decrease was on an average of 62 %. Only charcoal as clarifying substance proved effective, reducing the fenhexamide content by 91 %. Therefore, it is not surprising to find high fenhexamide residue if treatments are done just a few weeks before harvest. Fenhexamide is a recent pesticide, less toxic than other currently used fungicides in wineyards. The fenhexamid accepted daily intake (ADI) is 0.2 mg/kg/day. However, if acute toxicology is well documented for pesticides, there are always some lacks of data concerning chronic toxicology with low levels during a very long exposure period (10–20 years). Moreover, synergetic effects of mixture of pesticide or other organic residues on human health are completely unknown.

Therefore, it would be interesting to study more deeply this point in order to verify if the mean levels of fenhexamide would be decreased, by the use of a more easily degradable fungicide, by the use of lower doses or by establishing a longer withdrawal period between the last application and the vintage.

Preceding results corresponded to the sum of the pesticides found. Indeed, in modern wine growing a lot of substances are used at the time of several treatments. Therefore, we detected in wines not only one or two pesticides, but sometimes up to 9 different substances. Figure 3 shows the number of pesticides measured in Swiss

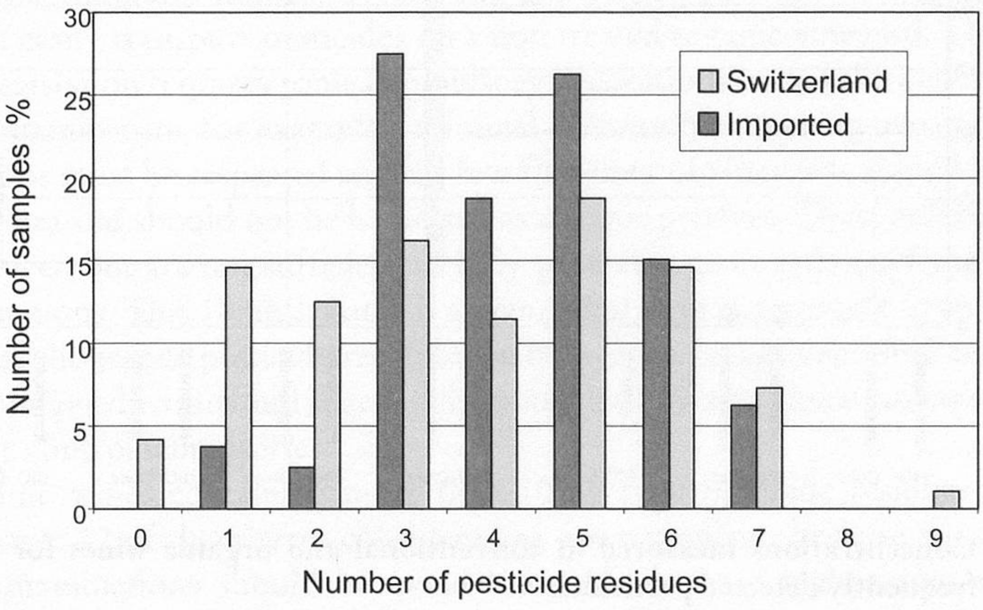

Figure 3 **Number of pesticides measured in Swiss and imported conventional wines**

and foreign wines. We observed that the majority of Swiss wines contained between 3 and 6 different substances, whereas the repartition is more homogenous for foreign productions. In fact, foreign wines produced in countries with climate similar to Switzerland (France, North-Italy) contained also a lot of pesticides. On the other hand, wines from warmer and dry countries such as California, Australia, South Africa, showed less pesticide residues. Again, more treatments are done in our regions to fight against fungic diseases. Moreover, in countries having an older wine growing tradition, the most part of these pesticides have been used for a long time and some parasites have acquired resistances in regard to some substances. Therefore, it is necessary to alternate substances with different mechanisms and/or appropriate mixtures in order to provide enough efficiency, and to avoid further resistances.

Organic wines

Unlike for conventional culture, the use of synthetic pesticides is totally forbidden in organic wine growing. 70 organic wines sold in the Geneva area market were analysed. Most of them were Swiss wines (52), particularly from Geneva producers, and the rest mostly from France and Italy.

Around half of the organic wines (33 samples) contained no detectable traces of pesticide residues and 29 samples only very low levels, below 10 µg/L. Traces in concentrations ranging between 10 and 34 µg/L were found in 8 samples. Figure 4 illustrates the overall results for Swiss wines and allows to compare the contamination between conventional and organic grown wines for some residues.

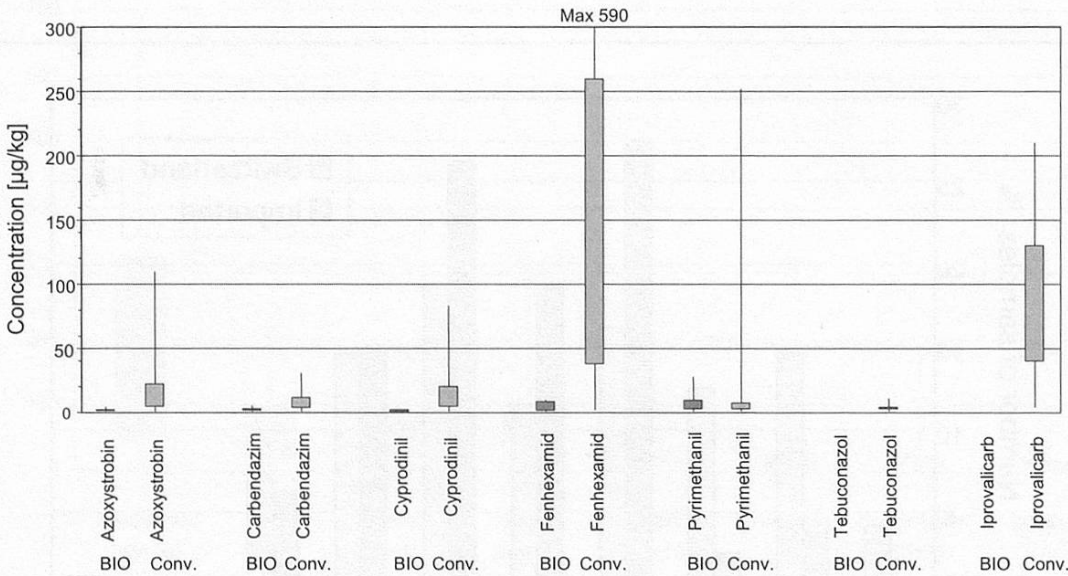

Figure 4 **Concentrations measured in conventional and organic wines for the most frequently detected pesticides.**
Rectangles represent 50 % of samples and the line indicates the minimum and maximum observed concentrations

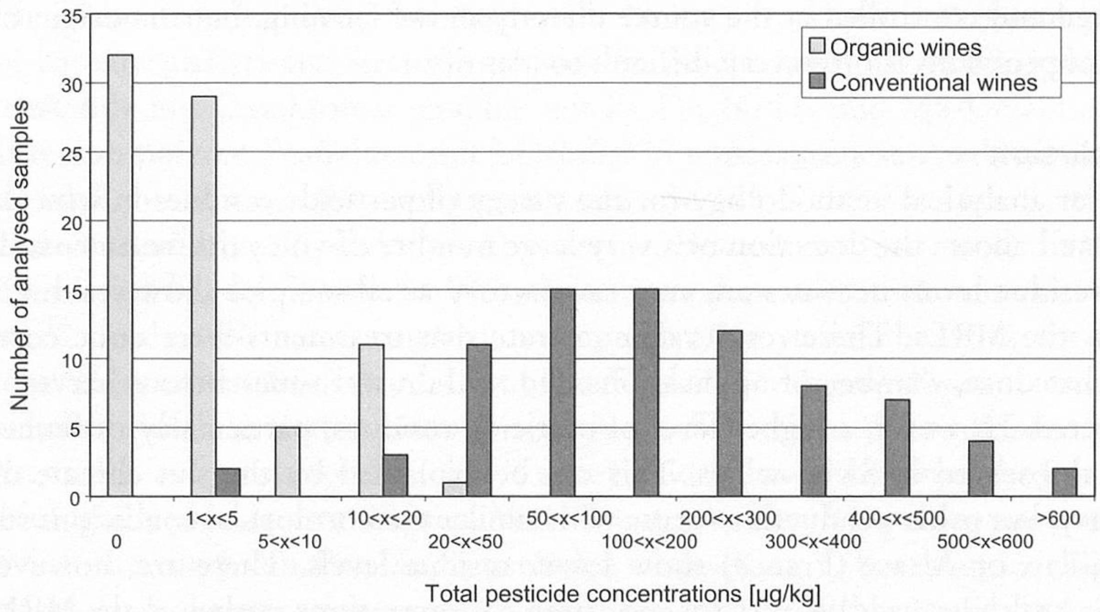

Figure 5 **Total pesticide residue concentrations measured in conventional and organic Swiss wines**

Figure 5 presents the measured concentrations of each residue for organic and conventional wines. These results are estimated as very satisfactory, because we observed that no organic wine producer used forbidden treatments with pesticides. Indeed, the levels of pesticide residues found in organic wines are much lower than those in conventional wines. Traces below 10 µg/L in organic wines are probably due to environmental contamination. This is almost unavoidable in such an exiguous territory as the Geneva area, where organic productions are often nearby conventional agriculture. Indeed, during the treatment of an agricultural parcel, the wind can easily transport pesticides on a non treated organic vineyard. The organic culture legislation requires some compulsory precautions to be followed in order to avoid contamination, for example a minimal distance between organic and conventional crops must be respected and the few first lines of vineyards should be used as buffer zones and should not be harvested as organic product. These rules are generally followed but are not sufficient to fully protect organic cultures from pesticide contaminations. This 10 µg/L value is an empirical limit determined from the background of thousands pesticide residues analyses done on conventional and organic agricultural productions and is generally recognized as contamination noise by food authority control laboratories.

Organic wines containing more than 10 µg/L of pesticide residues are more problematic. 12 of them were considered as not compliant, because we think that these contaminations should be avoidable. Indeed, these higher contaminations could come from insufficient distance between organic and conventional vineyards or from a bad separation between dies like pooled agricultural materials between organic and conventional wine producers. These contaminations could probably be reduced and controlled at the source directly in the farming, but the origin of this kind of problems is often very difficult to identify.

Conclusion

Our analytical methodology for the survey of pesticide residues in wine is efficient and allows the detection of a very large number of vineyard treatments. Pesticide residue levels in wines are very satisfactory as all samples show residue levels below the MRLs. These results demonstrate that treatments were done correctly and that dose, number of applications and withdrawal times before harvest were respected. However, a higher level of pesticide residues, particularly of fenhexamide, is observed in Swiss wines. This can be explained by the wet climate of our country, but other productions areas with similar meteorological conditions such as Beaujolais or Alsace (France) show lower residue levels. There are, however, no public health hazards because the measured concentrations are below the MRL. But if we consider the global concern due to pesticides exposure in food (pesticide content in fresh fruits and vegetables, in water, in oils, etc.) it would be interesting to reduce this level of fenhexamide, may be by using other more degradable fungicides or by prescribing longer withdrawal periods before the vintage.

Results about organic wines are satisfactory, because no organic wine producer used forbidden treatments with pesticides. We estimate that pesticide levels below 10 µg/L in organic wines are caused by environmental contamination. Higher contamination (higher than 10 µg/L, but below 35 µg/L), we consider as avoidable resulting from negligent application of neighbouring conventional farmers or directly in the farm by using equipment in pool with conventional farmers.

Acknowledgement

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Summary

Pesticide residue analysis in food remains a problem of public concern. Our laboratory has developed an analytical strategy with the complementary analysis of apolar pesticides by GC with ECD, NPD and MS detection and polar pesticides with LC-MS/MS. This methodology was applied to the survey of about 176 wines from conventional Swiss productions (particularly from the Geneva area) as well as from importations. We observed pesticide residues in 95 % of samples, but all were compliant to the Swiss legislation. For Swiss products, higher amounts of pesticide residues, particularly in fenhexamide were measured. Special attention was given to organic wines, and results of 70 samples are presented. We considered 12 wines as not compliant containing pesticide residues at levels higher than 10 µg/L. We observed some contamination problems, but no abuse with illegal use of pesticides.

Zusammenfassung

Die Pestizidanalytik von Lebensmitteln bleibt ein aktuelles Problem. Unser Labor hat eine analytische Strategie entwickelt, welche nebst der Prüfung auf apolare Pestizide mit Gaschromatographie mit ECD-, NPD- und MS-Detektion, die Analyse von polaren Pestiziden mit LC/MS/MS umfasst. Diese Analysenstrategie wurde im Rahmen eines Kontrollprogrammes von 176 Weinen aus konventionelle in- und ausländischer Produktion. Es war von besonderem Interesse, die Rückstandssituation bei den Schweizer Weinen, insbesondere aus dem Kanton Genf, und den ausländischen Weinen genauer zu untersuchen. Wir stellten bei 95 % der untersuchten Weinproben Rückstände fest. Die Rückstände lagen allesamt unter den gesetzlichen Toleranzwerten. Jedoch wiesen die Schweizer Weine höhere Rückstandsgehalte auf, insbesondere bei Fenhexamid. Unser Augenmerk galt auch den biologisch produzierte Weinen. Von 70 untersuchten Bioweinen mussten wir 12 Weine aufgrund von Pestizidrückständen über 10 µg/L beanstanden. Es liegt hier wohl ein Kontaminationsproblem vor, ein missbräuchlicher Pestizideinsatz im Biorebbau kann aber ausgeschlossen werden.

Résumé

L'analyse de résidus de pesticides dans les denrées alimentaires reste un problème d'actualité. Notre laboratoire a développé une stratégie analytique comprenant l'analyse complémentaire des pesticides apolaires par chromatographie gazeuse avec détection ECD, NPD et MS, et des pesticides polaires par LC-MS/MS. Ces analyses ont été appliquées à un programme de contrôle concernant 176 vins de production conventionnelle Suisse, et particulièrement genevoise, et les vins d'importation. Si nous observons des résidus de pesticides dans 95 % des échantillons, tous étaient conformes à la législation en vigueur. Nous avons toutefois constaté un niveau de concentration plus élevé en résidus, principalement en fenhexamide, dans les vins suisses. Nous avons également porté une attention particulière aux vins issus de l'agriculture biologique et les résultats obtenus pour l'analyse de 70 vins biologiques sont présentés. Douze vins biologiques contenant des résidus en pesticides supérieurs à 10 µg/l ont été considérés comme non conformes. Nous avons observé des problèmes de contaminations, mais pas de cas flagrant d'usage illicite de pesticides.

Key words

LC-ESI-MS/MS, tandem mass spectrometry, pesticide residues, wine analysis, organic wines

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