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ORIGINAL ARTICLE

Exposure to heavy metals due to pesticide use by vineyard farmers

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Abstract

Objectives To statistically analyze serum heavy metal levels in biological samples obtained from vineyard workers from southern Brazil and check for heavy metal exposure due to pesticide use.

Methods Serum samples were obtained from 54 farmers and 108 healthy unexposed individuals. Samples from the same farmers were obtained at three different time points over a 1-year period. Levels of lead, arsenic, nickel, zinc, manganese and copper were determined for each sample using dynamic reaction cell inductively coupled plasma mass spectrometry (DRC-ICP-MS). All results were statistically analyzed using the nonparametric Kruskal–Wallis test (followed by Dunn's post hoc test).

Results Results showed that serum heavy metal levels in farmers were twofold to fourfold higher than in controls. This difference was found for all heavy metals tested and was significant ($p < 0.05$). Serum metal levels among the farmers also correlated with the frequency of use of pesticides at a specific time of year, which varied according to seasonal conditions influencing the need for pesticide application.

Conclusions It can be concluded that in the vineyard region assessed, farmers were more susceptible to heavy metal exposure due to pesticide use.

Keywords Viticulture · Pesticides · Heavy metals · Occupational exposure

Introduction

Brazil is one of the world's largest grape producers. In 2012, Brazilian grape production was approximately 1,455,809 tons. Together with the states of Rio Grande do Sul, Pernambuco and São Paulo, the southern state of Paraná is a leading grape producer in Brazil. Also in 2012, Paraná alone harvested 70,500 tons of grapes (Alves et al. 2013; Mello 2013). This level of crop production, as is the case for any other crop in Brazil, is made possible by extensive use of pesticides, especially those based on heavy metals.

Copper is the main active agent employed in a range of products, being used in the forms of copper hydroxide, copper oxychloride, tribasic copper sulfate and copper oxide. However, copper is predominantly used as a mixture of copper sulfate and calcium hydroxide, commonly called "slaked lime." The resultant product works as a fungicide and is referred to as "Bordeaux mixture." Mainly as a result of Bordeaux mixture usage, copper levels both in soil and grapes are elevated in Brazilian vineyard areas (Kuhn 2011; Mirlean et al. 2007).

Heavy metal contaminants present in Bordeaux mixture as well as in other unrelated organic pesticides have been detected at high levels in other vineyard regions throughout the world, such as France, Italy, Croatia and Jordan

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(Al Nasir et al. 2001; La Pera et al. 2008; Leblanc et al. 2000; Orescanin et al. 2003). These metals include arsenic, lead, zinc and nickel, all of which can be harmful to human health if certain thresholds are exceeded. The same is true for copper. Some organic pesticides, even though they do not employ heavy metals as their active agent, contain these metals in their composition. Mancozeb, for example, is basically manganese dithiocarbamate forming complexes with zinc salts (La Pera et al. 2008).

Most farmers do not have the necessary training or educational level to safely handle pesticides (Bedor et al. 2009) and are subjected to exposure through inhalation and dermal contact (Baharuddin et al. 2011; Nuyttens et al. 2009). The application itself is also often not done properly, and high volumes of pesticides are applied incorrectly, leading to the contamination of crops as well as surrounding areas. Remnants of heavy metal pesticides might also persist in soil and be transferred to crop products, subsequently affecting consumers (Leblanc et al. 2000). Copper and other contaminant metals in areas previously under heavy pesticide use can be detected at levels 50 times higher than those of pesticide-free areas (Kuhn 2011). Arsenic and lead originating from lead arsenate, banned from the market half a century ago, can still be detected in areas that were under extensive pesticide use (Peryea and Creger 1994).

In the present study, blood samples were collected from a group of vineyard workers in the southern area of Brazil, and serum levels of lead, arsenic, nickel, copper, manganese and zinc were evaluated. Results were correlated with the use of pesticides during a specific period of the year.

Methods

Farmers from the vineyard region of northwestern Paraná were selected for this study. This area focuses on fine grape production, following a system of family-based farming on small properties. Visits to farmers occurred during events promoted by EMATER (Technical Assistance and Rural Extension Institute of Paraná), a local institution that organizes rural labor in the state of Paraná. The organization promoted events on three different dates, the first in November 2011, the second in February 2012 with the third and final event in August 2012. These periods were chosen based on the pattern of pesticide use, as informed by EMATER.

The project was presented to the farmers and those agreeing to take part signed an informed consent form in accordance with the Brazilian Ethics Committee (registered by the Committee under number CAAE 0375.0.093.000-11). Samples were collected from each individual farmer at all three contact time points. Only farmers attending all three events were considered valid for sampling. Also, only farmers working directly with grape farming were selected for sampling. Farmers present on all occasions but not cultivating grapes were excluded from the study. A total of 54 farmers participated in this study.

Prior to obtaining blood samples, all farmers filled out a simple form collecting subject data. Results were categorized according to gender, age and which pesticides were the most used. All blood samples were collected by conventional venous puncture and stored in previously decontaminated metal-free glass collection tubes. For decontaminating, all tubes were washed with running water and placed into a 10 % nitric acid solution for at least 48 h; tubes were then washed again with ultrapure Milli-Q water and dried at 40 °C. Tubes were stored without contact with dust or metallic surfaces. Subsequently, samples were centrifuged at 10,000 rpm for 10 min to separate serum from other blood elements. Serum as a matrix was preferred over more commonly used whole blood or urine because samples were obtained at three different time points and long storage periods were unavoidable, a factor that could lead to variations in later metal analyses.

In order to obtain controls for the study, samples from 108 healthy blood donors were collected. The control subjects were volunteers selected from the local teaching hospital blood center (University Hospital of Maringá). Volunteers also filled out a simple form to determine age, gender, occupation and origin. Control samples were treated in the same way as farmers' samples. All control individuals were chosen based on farmer profile: for each vineyard worker of a given age and gender, two healthy individuals matched for age and gender were selected to serve as controls; this ensured the sex and age distribution of the control group reflected that of the farmer group. Also, to ensure control group selection would not influence results, only individuals not working under conditions that could be considered modifiers of metal exposure were selected. Both farmer and control populations also differed in as far as the blood center was located in a city 30 km away from the main vine production area studied. Thus, the individuals selected for the control group were not exposed to metals due to direct air and soil contamination derived from pesticide use. Samples from unexposed control individuals were obtained within the period spanning from January to June 2013.

All serum samples were fractionated as triplicates into three different tubes at a volume of 100 μL and sent to the Laboratory of Metal Essentiality and Toxicology at the University of São Paulo, Brazil. This laboratory employs a technique for fast determination of heavy metals in serum utilizing dynamic reaction cell inductively coupled mass spectrometry (DRC-ICP-MS) using reference standardized matrices provided by the L'Institut National de Santé Publique du Quebec (Canada). These were checked prior to sample analysis to validate the method and ensure quality assessment of the analysis protocols used (Batista et al. 2009). Each serum sample was screened for lead, arsenic,

Table 1 Frequency of pesticide use according to vineyard farmers assessed

Active compound	Chemical class	N	%
Copper oxychloride/copper sulfate	Inorganic	38	70.4
Mancozeb	Dithiocarbamate	35	64.8
Fenarimol	Pyrimidinyl carbinol	25	46.3
Glyphosate	Substituted glycine	20	37.0
Methamidophos	Organophosphate	19	35.2
Zoxamide and cymoxanyl	Benzamide and acetamide	18	33.3
Azoxystrobin and cyproconazole	Strobilurin and triazole	17	31.5
Metiran and pyraclostrobin	Strobilurin and dithiocarbamate	10	18.5
Imidacloprid	Neonicotinoid	9	16.7
Tebuconazole	Triazole	7	13.0
Zeta-cypermethrin	Pyrethroid	7	13.0
Folpet	Dicarboximide	6	11.1
Thiophanate-methyl	Benzimidazole	6	11.1
Benalaxyl and mancozeb	Acylalanine and dithiocarbamate	5	9.3
Captan	Dicarboxamide	5	9.3
Copper hydroxide	Inorganic	5	9.3
Formetanate hydrochloride	Phenyl methylcarbamate	3	5.6
Difenoconazole	Triazole	3	5.6
Sulfur	Inorganic	3	5.6
Fenamidone	Imidazolinone	3	5.6
Metalaxyl-M and mancozeb	Acylalanine and dithiocarbamate	3	5.6
Abamectin	Avermectin	2	3.7
Flubendiamide	Phthalic acid diamide	2	3.7
Ammonium glyphosate	Substituted homoalanine	2	3.7
Methomyl	Oxime methylcarbamate	2	3.7

Pesticides are named according to active chemical compound and their chemical class. Commercial names are not included. Percentages refer to proportion of the total 54 farmers assessed

nickel, manganese, zinc and copper. After the last sample was processed, all samples were analyzed at the same time during the period of June–July, 2013.

Results for serum heavy metal levels were then statistically analyzed using the software GraphPad Prism 5.0®. Kruskal–Wallis tests followed by Dunn's post hoc test were conducted to determine any differences in serum metal levels by comparing control and vineyard worker groups considering the interval between the three different sample collection times.

Results and Discussion

Prior to sample collection, participants completed a form giving basic identification details and most frequently used pesticides. Farmers were asked about pesticides in general. Most respondents reported the commercial name of the pesticides used while a few named the active ingredients. The results are shown in Table 1 which lists compound type, class and number of farmers citing the use of each specific pesticide.

Different preparations of copper compounds were reported by 70.4 % of the farmers and mancozeb, a dithiocarbamate prepared with zinc and manganese salts, was cited by 64.8 %. Other compounds, such as the fungicide fenarimol, the herbicide glyphosate and the organophosphate methamidophos were also reported to some extent, being used by 46.3, 37.0 and 35.2 % of farmers, respectively. Several other pesticides were also mentioned by more than 20 % of the farmers, and numerous preparations were cited by a small number of participants. However, these other compounds are present in pesticide formulations that do not contain heavy metals.

Among the most used pesticides, copper-based products were cited often, such as copper oxychloride and copper sulfate. Copper oxychloride is a simple preparation sold under the commercial names Cupuran® and Recop®. Copper sulfate, on the other hand, has been used for decades mixed with calcium hydroxide, forming the so-called Bordeaux mixture, a highly effective fungicide. It has been reported that copper preparations used in viticulture not only contaminate grapes and soil with high levels of copper, but also contain other contaminant metals, such as lead, arsenic, zinc, chromium, cadmium and nickel (Kuhn 2011; Mirlean et al. 2005). The second most used pesticide was mancozeb; this pesticide is a dithiocarbamate, not inorganic alone, but prepared with manganese and zinc salts. It is crucial to determine exactly which types of pesticides are employed by the farmers in order to ascertain whether the preparations contain heavy metals. Since copper-based pesticides and manganese- to zinc-containing preparations are the most commonly handled products by this population of vine farmers, it is reasonable to expect increased levels of these metals in farmers' serum.

Serum samples were collected on each of the three visits made to the farmers: November 2011, February 2012 and August 2012. Farmers´ results were compared against their respective controls and also to each other, independently of controls to verify potential differences due to sampling at different times of year. Kruskal–Wallis followed by Dunn's multiple comparison tests were performed to analyze the data. The results are summarized in Table 2.

As confirmed by Kruskal–Wallis and Dunn's post hoc tests (Table 2), serum levels for all metals across all three visits differed compared with the results obtained for the control group. Results obtained from the first and second visits did not differ statistically from each other but were statistically different from results of the third visit.

Table 2 Serum heavy metal levels of grape farmers grouped by visit compared with control group

Metal analyzed	Controls	First visit	Second visit	Third visit
Lead (μg/L)	0.23 (0.328, 0.564)[b,c,d]	1.5 (1.31, 1.81)[a,d]	1.521 (1.49, 2.00)[a,d]	0.787 (0.700, 1.08)[a,b,c]
Arsenic (μg/L)	1.135 (1.11, 1.27)[b,c,d]	3.369 (3.26, 3.48)[a,d]	3.776 (3.61, 3.77)[a,d]	2.07 (2.10, 2.36)[a,b,c]
Nickel (μg/L)	0.6045 (0.602, 0.883)[b,c,d]	2.484 (2.45, 3.18)[a,d]	2.686 (2.55, 2.98)[a,d]	1.256 (1.41, 2.016)[a,b,c]
Manganese (μg/L)	0.514 (0.510, 0.645)[b,c,d]	1.597 (1.62, 2.10)[a,d]	2.048 (1.97, 2.35)[a,d]	1.181 (1.20, 1.72)[a,b,c]
Zinc (μg/L)	714.8 (680.6, 759.7)[b,c,d]	1298 (1246, 1375)[a,d]	1442 (1375, 1480)[a,d]	1060 (1008, 1126)[a,b,c]
Copper (μg/L)	961.8 (947.2, 1097)[b,c,d]	1747 (1775, 2007)[a,d]	1939 (1973, 2255)[a,d]	1384 (1379, 1641)[a,b,c]

Results for control and farmer groups are expressed as medians with respective upper and lower 95 % confidence intervals in parentheses

[a] Significantly different from control group

[b] Significantly different from results obtained on first visit

[c] Significantly different from results obtained on second visit

[d] Significantly different from results obtained on third visit. Results considered significant based on a p value < 0.05

The pattern of exposure on each visit can also be observed. For all metals analyzed, serum levels were roughly twofold to fourfold higher on the first and second visits compared with the control group. On the third visit, however, serum heavy metal levels were only approximately 1.5-fold to twofold higher than the control group. The first and second visits were made in November 2011 and February 2012, respectively; at this time of year, grapes are heavily pulverized with pesticides, according to reports by the farmers. The third visit occurred in August 2012 when pesticide usage is lower. During winter time, spanning from June to August in the Southern hemisphere, the lack of rainfall and heat makes the crops more resilient due to the absence of pests. Consequently, the plants do not require as many pesticide pulverizations as during the summer, spanning from November to February (Bloomfield et al. 2006). Since serum analysis generally detects recent exposure to heavy metals, the results obtained serve as a good indicator of the actual amounts of pesticides used.

Other authors have also measured the effects of vine farming on heavy metal exposure profile and found similar results to those of the present study. Australian vineyard workers engaged in activities where copper-based pesticide exposure was expected to be high had elevated levels of copper as detected in buccal cells. This result is in accordance with the findings of the present study, where concentrations of not only of copper, but all the other metals assessed, in biological samples were high among farmers more directly involved with pesticide handling (Thompson et al. 2012). In Croatia, vineyard workers exhibited greater respiratory dysfunctions in comparison with a control group, although heavy metals were not screened in biological fluids. The authors suggested that pesticides and heavy metals might implicate in these respiratory problems, indicating that these factors in vine farming might trigger deleterious effects on health (Zuskin et al. 1997).

Pesticides are certainly a source of heavy metal contamination in vine farming, especially copper, but other factors may also contribute to heavy metal exposure. As previously mentioned, Bordeaux mixture and mancozeb are direct sources of copper, zinc and manganese. Copper preparations can also contain lead and nickel as contaminants (Kuhn 2011; La Pera et al. 2008; Mirlean et al. 2005; Mirlean et al. 2007). Arsenic and lead were also used extensively in the past as pesticides (mostly combined as lead arsenate), and although now banned and no longer in use, such metals can still be detected in soils planted with crops treated with these pesticides (Järup 2003; Peryea and Creger 1994). Only a single study reporting nickel as a contaminant of copper preparations was found; there is a dearth of reports in the literature correlating nickel contamination with pesticide use (Kuhn 2011). The present study supports the premise that nickel is a residual pesticide contaminant, but further studies should be conducted to confirm this theory.

A study performed in the USA evaluating urinary levels of metals in farmers of Mexican origin revealed arsenic and lead levels higher than reference values. The studied population comprised farmers in general, not only vineyard workers, and the authors indicated that metal exposure might be due not only to pesticide exposure, but also to environmental contamination in general and other habits such as smoking (Quandt et al. 2010). Another study demonstrated that soils in rural areas located near industrial and mining areas contained concentrations of copper, lead and arsenic twice as high as non-contaminated areas (Loska et al. 2004). Other authors showed that other factors can influence pesticide exposure, such as diet and use of cosmetics containing metals (Al-Saleh et al. 2009; Leblanc et al. 2000). This shows that the problem of metal exposure due to farming goes beyond pesticide exposure. In the present study, vine farmers and control subjects were not screened for habits such as smoking or consumption of pesticide-free foods; therefore, variations due to these factors cannot be ruled out. Moreover, while exposure to heavy metals involves several variables that are not assessable at all times, this study demonstrated that pesticide exposure strongly correlated with increased metal levels in farmers compared with a non-rural population not directly exposed to heavy metals from pesticide handling. While other factors influence metal exposure, direct handling of pesticides is a more evident factor among vine farmers.

Blood and urine have traditionally been favored over serum for direct metal analysis. In recent years, efficient new methods have arisen as more sensitive and robust techniques, such as DRC-ICP-MS. This technique is capable of detecting several metals concomitantly at trace concentrations with high precision and reliability in any matrix, given proper sample dilution and treatment. The reliability of screening serum using DRC-ICP-MS for metal analysis has been demonstrated in a number of studies, validating its use as a viable matrix (Batista et al. 2009; D'Ilio et al. 2006; Goullé et al. 2005; Nischwitz et al. 2008; Nunes et al. 2010). Indeed, considering the present experimental design, use of such traditional matrices would not necessarily be the best option. Urine, while useful as a noninvasive matrix, is more useful in cases where evaluation of long-term and cumulative exposures is required. It can also be argued that serum better reflects metal absorption, and thus correlates more closely with possible toxic effects and recent exposure, especially for lead. Whole blood, although considered the primary matrix for direct metal analyses, must be assessed shortly after collection, as hemolysis does not allow it to be frozen or refrigerated permitting metabolic processes to continue and possibly change the matrix. Serum does not suffer from this limitation, and sample storage was unavoidable in the present study (Barbosa et al. 2005; Batista et al. 2009; Ehresman et al. 2007). Nonetheless, while serum is certainly viable as a matrix for heavy metal analysis, more studies are needed to determine the extent to which heavy metal levels in serum mirror those of blood and urine.

Conclusions

In the vineyard area assessed, farmers were more susceptible to heavy metal exposure due to pesticide use than non-farmers. This heavy metal exposure correlated positively with the amount of pesticides used at a specific time of year. The presence of heavy metals in viticulture areas is well documented, but there is a lack of studies on the exposure profile of vineyard workers. This study can contribute by bridging this gap but further investigations assessing the amount of contaminant metals in farmers using biological sampling are necessary.

Conflict of interest The authors declare that they have no conflict of interest.

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