Pollution of vineyards by atmospheric leada

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(Manuscript received 1 November 1974 and accepted 7 February 1975)

Lead accumulation in vineyards exposed to automobile exhaust gases has been studied by means of three indicator materials (grapes, leaves and soil) sampled at increasing distance from the source. The regression analysis of concentration data on the logarithm of the distance, based on an accepted model, shows that these three materials are suitable for detecting the extent of pollution. Far from the source, where the polluting effect is negligible, the mean typical levels of lead in these materials are 0.43, 6.7 and 16.2 μg/g dry weight respectively. The contribution of the atmospheric lead to the pollution of plant materials, at various distances from the source, is thus simply evaluated. The surface contamination for grapes and leaves is also discussed.

1. Introduction

From some time it has been found that the tops of plants growing near roads contain an excess of lead due to the accumulation of atmospheric lead from automobile exhaust gases on the plant surface.1-8 A preliminary study on grapes has already indicated that there is a marked species sensitivity to the pollutant. The extent of pollution may be evaluated on the basis of an approximate model describing the concentration of lead in grapes as a function of the distance from the source.9-11

In this paper the results of a systematic study on grapes, leaves and soil are reported. This study has been planned in order to select the best material for the pollution control. Regression analysis has been adopted as a statistical tool for decision making. As in previous researches the test site is an area situated near Angoris (Cormons, Gorizia) which is particularly suitable for these investigations.

2. Experimental

2.1. Materials and sampling methods

2.1.1. Grapes

Sampling has been restricted to Traminer wine grapes, which were taken at ripening, a day before vintage, at distances from 13 to 183 m from the source. The grapes sample includes six bunches taken from two plants and collected at 1.5 m from the ground. Chemical analysis was performed on the berries (average moisture content 84%).

a Research performed with the financial support of Consiglio Nazionale delle Ricerche, Roma, Contract N.73.00406.10.
2.1.2. Leaves
Samples of ten fully developed leaves have been collected from the same plants near
the bunches (average moisture content 71%).

2.1.3. Soils
From an area of approximately 0.5 m², 250 g of material has been sampled near the
surface (5–10 cm under the ground). Pedologically the soil is a terrae rossa containing
remnants of the original calcareous gravels, which had been previously eliminated, together
with macroscopic organic débris, by picking up on a sieve of 1 mm mesh size. An aliquot has been reduced to
pass a 0.125 mm mesh sieve in an agate mortar (average moisture content 4%).

2.2. Lead determination methods
The method for the extraction and the determination of lead by atomic absorption
spectroscopy from a charred sample of grapes has been already described. The same
method has been applied to leaves by reducing the sample weight to 1 g of dry material.

The method for soil is simply based on the solubilisation of lead at pH 1.0 with an
excess of 0.1 M nitric acid. Aerosol particles from the exhausts are in fact readily acid-
soluble because they are predominantly mixtures of solid phases of lead oxocarbonate,
oxides and carbonate which originate on ageing. Figure 1 shows that the con-
centration of acid-leached lead reaches a maximum at pH 1–1.2 in this soil.

The procedure is as follows. An aliquot of 0.500 g of dried sample (at 105 °C) is
transferred into a 50 ml calibrated flask, which is made up to the volume by 0.10 M
nitric acid (ex Aristar BDH). The suspension is shaken overnight, 40 ml of the clear
solution, obtained by centrifugation or by filtration through a 5 cm Schleicher and

Figure 1. Lead (cPb, μg/g dry weight) leached from two terrae rossa soil samples at various pH
(at equilibrium). 1, Sample at d=13.8 m. 2, Sample at d=64.6 m. The dark point corresponds
to the value 17.7 ± 1.0 μg/g (mean and root mean square deviation from five analyses). Arrows
indicate the maximum leachable lead under strong acid attack, that is with an excess of HNO3 N for
5 h at 100 °C [sample 1:35.8 μg/g; sample 2: 18.3 ± 1.1 (three analyses)].
Pollution of vineyards by lead

Schüll 589\textsuperscript{1} paper disc, is filtered through a Mitex 0.8 \(\mu\)m Millipore micromembrane filter by means of a 36 mm diameter Swinnex device and a plastic syringe. Three 10.00 ml aliquots of the ultrafiltered solution are then transferred in three 25 ml volumetric flasks. To two of the latter are added 0.300 and 0.500 ml of the standard solution containing 5.00 \(\mu\)g/ml of lead in 0.1 M nitric acid; this solution is obtained daily from a standard stock solution of 500 \(\mu\)g/ml (from metallic lead ACS certified Fisher). A reagent blank is prepared in parallel. The solutions are then made up to the volume with 0.10 M nitric acid and are extracted with 1.00 ml of \(n\)-heptanone (BDH), after the addition of 0.50 ml of 4\% aqueous ammonium pyrrolydinedithiocarbamate solution (freshly prepared from BDH reagent).

The organic extract is filtered through a 0.5 \(\mu\)m Mitex filter (Millipore), mounted on a 0.5 ml Teflon lined syringe (Hamilton), and analysed on an atomic absorption spectrophotometer (Perkin Elmer 290 B) with an air-acetylene flame with a 10 cm optical path length (titanium burner). The gas flows are optimised for the organic solvent. The analysis is carried out at 283.3 nm (Intensitron lamp) using a spectral slit width of 0.7 nm. Readings are recorded taking as zero the extract of the blank. The required concentration is determined analytically on a desk processor (Olivetti 101) using a least-squares program with the \(F\)-test of significance for the linear regression. A few analyses were rejected and repeated as \(F\text{(obs)} < F\text{(theor.)} = 161\) for \(v_1 = v_2 = 1\) degree of freedom at \(P = 0.95\).

With this procedure, the extraction of lead from aqueous to organic phase is performed at pH 1.0–1.2 and it is maximum for this two-phase system. The intra-laboratory reproducibility expressed as the coefficient of variation has been found to be \(\pm 6\%\) at the levels of lead encountered in this soil. Iron does not interfere, at least at the concentration observed in soil solutions.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Lead content (\(c_{\text{Pb}}\) \(\mu\)g/g dry weight) in grapes (1), leaves (2) and soil (3) of Traminer vineyards as a function of the distance (\(d\), metres) from the centre of the road (for further details see the text). A point at \(d = 13.8\) m, \(c_{\text{Pb}} = 2.33\) \(\mu\)g/g is out of diagram (1).}
\end{figure}
Table 1. Parameters of the fitting curve $c_{po} = a + b \log_{10} d + c \left(\log_{10} d\right)^2$; analysis of the variance for the regression and runs test on the residuals

<table>
<thead>
<tr>
<th>Material</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>Root mean square deviation</th>
<th>Source of variation</th>
<th>Degrees of freedom</th>
<th>Sum of squares</th>
<th>Variance</th>
<th>obs.</th>
<th>$F$ calc. ($P=0.01$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grapes</td>
<td>9.797</td>
<td>-10.00</td>
<td>2.644</td>
<td>± 0.17</td>
<td>Attributable to regr.</td>
<td>2</td>
<td>4.9413</td>
<td>2.4707</td>
<td>80.8</td>
<td>5.14</td>
<td>0.80</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Deviation from regr.</td>
<td>40</td>
<td>1.2223</td>
<td>0.0306</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Total</td>
<td>42</td>
<td>6.1636</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leaves</td>
<td>68.55</td>
<td>-65.77</td>
<td>17.27</td>
<td>± 1.21</td>
<td>Attributable to regr.</td>
<td>2</td>
<td>231.4537</td>
<td>115.7269</td>
<td>78.5</td>
<td>5.12</td>
<td>0.79</td>
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<td></td>
<td>Deviation from regr.</td>
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<td>60.4540</td>
<td>1.4745</td>
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<td></td>
<td>Total</td>
<td>43</td>
<td>291.9077</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td>118.30</td>
<td>-100.90</td>
<td>24.81</td>
<td>± 2.04</td>
<td>Attributable to regr.</td>
<td>2</td>
<td>958.6557</td>
<td>479.3279</td>
<td>114.7</td>
<td>4.33</td>
<td>0.86</td>
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<td></td>
<td>Deviation from regr.</td>
<td>36</td>
<td>150.4278</td>
<td>4.1785</td>
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<td></td>
<td></td>
<td></td>
<td>Total</td>
<td>38</td>
<td>1109.0835</td>
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</tr>
</tbody>
</table>

Runs test on the residuals

<table>
<thead>
<tr>
<th>Material</th>
<th>$n_{+}$</th>
<th>$n_{-}$</th>
<th>$r$</th>
<th>$\mu$</th>
<th>$\sigma$</th>
<th>$\bar{u}$</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grapes</td>
<td>23</td>
<td>20</td>
<td>12</td>
<td>22.39</td>
<td>3.22</td>
<td>-3.05</td>
<td>0.001</td>
</tr>
<tr>
<td>Leaves</td>
<td>23</td>
<td>21</td>
<td>21</td>
<td>22.95</td>
<td>1.03</td>
<td>-1.40</td>
<td>0.08</td>
</tr>
<tr>
<td>Soil</td>
<td>20</td>
<td>19</td>
<td>18</td>
<td>20.48</td>
<td>3.03</td>
<td>-0.643</td>
<td>0.23</td>
</tr>
</tbody>
</table>
2.3. Statistical data processing

The chemical analyses were performed on coded samples taken at random (three operators). Regression analyses of concentration data on distance from the source were performed on the basis of a parabolic model of the type: 

$$c_{pb} = a + b \log_{10} d + c (\log_{10} d)^2,$$

where $a$, $b$ and $c$ are constants, $d$ is the distance (m). A standard multiple linear regression program on the CDC 6200 processor (Centro di Calcolo, Università di Trieste) was utilised. Dispersion of data around the interpolating line was studied by the analysis of the variance for the regression, using $F$ and $R^2$ ratios as criteria of adequacy. Residuals were examined by graphical procedures and by the runs test for randomness.\(^{15}\)

3. Results and discussion

Figure 2 shows the lead content ($c_{pb}$ in μg/g dry weight) in the grapes, leaves and soil samples as a function of the distance ($d$ in metres) from the source. These data belong to the sampling trip of September 1973, and are fitted by the parabolic curve (continuous line). Root mean square deviation of estimate is graphically presented as broken lines above and below the interpolating curve.

Table 1 summarises the parameters of the parabolic curve observed in various materials and the analysis of the variance for the regression. The deviation from regression accounts for 15–20% of the total sum of squares. Therefore in all cases the parabolic model largely fits the observed points, in accordance with previous observations.\(^5,10\)

The adequacy of the model has also been tested by the examination of residuals. The runs test applied to the space sequence of residuals shows that in leaves and soil the arrangement of signs is random, therefore substantiating the model. In grapes the probability (0.1%) corresponding to the value of $-3.06$ in the cumulative normal distribution function is too low for accepting the randomness hypothesis. The parabolic model is actually inadequate to interpolate the observed points beyond the apex of the curve: the model function is increasing, whereas the observed points just oscillate around the typical content of lead in the material. For the $c_{pb}$ values with $d > d_A$ (distance corresponding to the abscissa of the apex), the polluting effect of the source may be neglected and the mean typical content ($c_T$) may be determined (see Table 2). The evaluation of the contribution of the atmospheric lead to the pollution of plant materials, at various distances from the road, is therefore trivial (see Table 3).

On the basis of the specific surface of both materials,\(^a\) the surface contamination may be very roughly evaluated. As is expected for materials having nearly the same exposure to the atmospheric lead, the surface contamination of the materials is of the same order, although it is systematically 20% lower in leaves than in grapes. This error reflects mainly the inaccuracy involved in the underestimation of leaf surface.

Although data are not available, the parabolic model is certainly inadequate for $d < 10$ m, where it predicts a rapid increase in $c_{pb}$ values. Actually the appearance of a

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\(^a\) The surface of round berries was simply assessed by their mean diameter measured from a 35 berry sample taken from various bunches. The surface of the leaves was evaluated by tracing the leaf contour on a sheet of paper and planimetrically measuring the projected area.
Table 2. Typical level of lead (CT, μg/g dry weight) in some materials from Traminer vineyards; s, root mean square deviation calculated from n values having d>dA; dA, distance (m) corresponding to the abscissa of the apex; cA, concentration of lead (μg/g dry weight) at the apex

<table>
<thead>
<tr>
<th>Material</th>
<th>dA</th>
<th>cA</th>
<th>n</th>
<th>CT ± s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grapes</td>
<td>78</td>
<td>0.33</td>
<td>16</td>
<td>0.43 ± 0.07</td>
</tr>
<tr>
<td>Leaves</td>
<td>80</td>
<td>5.90</td>
<td>16</td>
<td>6.7 ± 1.0</td>
</tr>
<tr>
<td>Soil</td>
<td>108</td>
<td>15.70</td>
<td>9</td>
<td>16.2 ± 1.0</td>
</tr>
</tbody>
</table>

Table 3. Surface contamination [(cPb-CT)/S, μg/cm²] of lead in plant materials; d, distance (m) from the source; cPb, interpolated concentration and cT, typical mean level (μg/g dry weight); S, specific surface of the material (cm²/g)

<table>
<thead>
<tr>
<th></th>
<th>cPb-CT</th>
<th>(cPb-CT)/S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grapes</td>
<td>Leaves</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1.26</td>
<td>8.4</td>
</tr>
<tr>
<td>20</td>
<td>0.82</td>
<td>5.5</td>
</tr>
<tr>
<td>30</td>
<td>0.36</td>
<td>2.4</td>
</tr>
</tbody>
</table>

*a Estimated only as a projected area.

maximum at d=0 seems to be quite reasonable. Further studies are still in progress in testing models which are more compatible with the physical evidence.

Acknowledgements

The authors are grateful to Professor C. Calzolari for his encouragement in several ways. The assistance of the manager of SATCA (Angoris), Dr A. Locatelli, in providing grape samples is also gratefully acknowledged.

References