Tree death

Is lead killing German forests?

from M.H. Unsworth and R.M. Harrison

WIDESPREAD reports that trees in the forests of central Europe are damaged and dying have stimulated many hypotheses into the possible causes. Sulphur dioxide or acid rain alone do not seem to provide explanations of the distribution and symptoms of injury. Much attention at present is devoted to the possible interaction of ozone (generated photochemically in the lower atmosphere) and acidic deposition as stress factors; there are also unsubstantiated press reports that a plant virus is associated with damaged trees but not with healthy ones. Although there is speculation that damage may be caused by hitherto unrecognised trace components of the atmosphere or of rain, there have been few reports that any such substances are found in concentrations injurious to plants. On page 714 of this issue, H. Faulstich and C. Stournaras¹ now report that concentrations of trialkyl-lead in rainwater collected in the Black Forest of Germany are close to those known to kill plant and animal cells. If this is correct, it suggests that lead additives to motor fuel are directly associated with tree damage. But in our view there are strong reasons for disbelieving this interpretation.

Lead is added to gasoline (petrol) in the form of organic tetraalkyl-lead (TAL) compounds, mostly tetramethyl-lead and tetraethyl-lead, but exhaust gases contain predominantly inorganic lead aerosol. TAL vapour enters the atmosphere in small amounts through evaporation of gasoline and from exhaust pipes as unburned fuel. TAL concentrations in urban air are typically about 50 ng m⁻³, that is, about 5% of the total lead concentration of 1 µg m⁻³. In the atmosphere, TAL is eventually converted to inorganic lead with the intermediate formation of trialkyl-lead (TriAL). If the organic compounds are not removed to the ground, the ratio of TriAL/TAL concentrations is expected to increase with distance downwind from the source. Atmospheric dispersion, however, dilutes polluted air, so that air concentrations of all lead compounds derived from gasoline are lower in rural than in urban areas.

Until recently, lack of sufficiently sensitive analytical techniques has meant that the presence of TriAL in urban and rural air has had to be inferred either from the difference between total organic lead and TAL in air^{2,3} or from any TriAL in rainwater; estimates suggest that TriAL concentrations in rural air are less than 2 ng m⁻³. In contrast, there have been several studies of TriAL in rainwater. Since its salts are fairly soluble in water, scavenging processes in cloud and by precipitation undoubtedly provide an important sink

for removing TriAL from the atmosphere. Measurements of lead concentration in rainwater are summarized in the table. These results were obtained by three different methods: selective extraction and lead-specific detection⁴; a lead-specific gas chromatography/atomic absorption procedure^{5,7}, and a bioassay procedure for analysis of trialkyl-lead based on inhibition of tubulin polymerization in pig brain¹. The table reveals that the TriAL measurements from the Black Forest¹ are 100–1000 times larger than those from elsewhere. Are these observations correct or is the analytical method at fault?

For several reasons we find the new observations of TriAL anomalous. To

annual deposition of TriAL comparable the total amount of lead annually added to gasoline in Germany.

Rather than seek unusual mechanisms for generating and depositing TriAL in Germany, it seems more likely that the bioassay method used by Faulstich and Stournaras is subject to interferences by other constituents of rainwater. A wide range of chemicals can inhibit the tubulin polymerization process⁸, including halothane and other anaesthetic drugs, as well as organomercurials such as methylmercury. The minor-component composition of rainwater is not well established but methylmercury and dimethylmercury, as well as many halocarbons, are certainly present in the atmosphere. The more polar compounds are no doubt also present in rainwater and it is highly likely that interferences will arise in the analytical procedure. Moreover, the method uses evaporation to concentrate rainwater samples and, if high temperatures were

Concentrations of trialkyl-lead and total lead in rainwater

Sampling location	Trimethyl-lead (ng l ⁻¹)	Triethyl-lead (ng l ⁻¹)	Total lead (µg l ⁻¹)	Reference
Central Antwerp Highway (Belgium)	58–330*		152–386	4
Residential (Belgium)	45–88*		148–214	4
Rural (Belgium)	40–64*		86–150	4
University campus (Belgium)	28*		29	4
Downtown (Belgium)	22	10	133	5
Rural (UK)	45	26	280	5
Various sites (UK)	23	42	14	6
Black Forest (Germany)	10–31	29–71	5–34	7
	<2,000–62,000*		<2–210	1

*Data correspond to total trialkyl-lead

account for such high concentrations in rain would require very high atmospheric concentrations of TriAL. It is not possible to make precise calculations because chemical kinetic information is lacking, but if typical values elsewhere of (TriAL)_{air}/ (TriAL)_{rain} are (2 ng m⁻³)/(50 ng l⁻¹), then simple proportionality implies that air concentrations of 80–2500 ng m⁻³ TriAL should be associated with the rain in the Black Forest. Such high concentrations of organic lead in air are found, very occasionally, but only close to gasoline filling stations² where they would be dominated by water-insoluble TAL. Mechanisms of atmospheric dispersion and rain production in clouds would not allow such concentrations in widely distributed rainfall.

The proportions of TriAL to total lead reported by Faulstich and Stournaras are unusual; the other studies listed in the table indicate that less than 1% of the total lead is in the TriAL forms. In the Black Forest, although total lead in rain is comparable to that at other non-urban sites, the proportion in the TriAL form is apparently 30–50 per cent. We cannot think of any plausible combination of exhaust emissions and deposition processes that would allow such a proportion to arise. If this occurred regularly in rain throughout Germany, it would imply an

used, many trace constituents, including TriAL, would have been broken down.

Although, in our view, the proposition that trialkyl-lead occurs in toxic concentrations in rain is entirely unproven, the fact remains that Faulstich and Stournaras appear to have observed some factor in rainwater that inhibits tubulin polymerization. If this is shown to be the case in further experiments, it should stimulate both the search to identify the mysterious factor in German rain and attempts to quantify its toxicity. □

1. Faulstich H. & Stournaras, C. *Nature* 317, 714 (1985).
2. de Jonghe, W.R.A., Chakraborti, D. & Adams, F.C. *Envir. Sci. Technol.* 15, 1217 (1981).
3. Harrison, R.M., Radojević, M. & Hewitt, C.N. *The Science of the Total Environment* 44, 235 (1985).
4. de Jonghe, W.R.A., van Mol, W.E. & Adams, F.C. *Proc. Int. Conf. Heavy Metals in the Environment* (CEP Consultants, Edinburgh, 1983).
5. Chakraborti, D. *et al. Anal. Chem.* 56, 2692 (1984).
6. Harrison, R.M. & Radojević, M. *Envir. Technol. Lett.* 6, 129 (1985).
7. Harrison, R.M., Hewitt, C.N. & Radojević, M. *Proc. Int. Conf. Heavy Metals in the Environment* (C.E.P. Consultants, Edinburgh, 1985).
8. Faulstich, H., Stournaras, C., Doenges, K.H. & Zimmerman, H.P. *FEBS Lett.* 174, 128 (1984).

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H. Faulstich and C. Stournaras will respond to this article within a few weeks.