Effects of changing to unleaded petrol on traffic related emissions. Trace metal and lead isotopic evidence for increased pollution

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In the late eighties, import of cars using high concentrations of alkyl-lead containing fuel was abandoned in the Netherlands. In addition the amount of alkyl-lead in petrol was significantly lowered. In 1997, lead was totally replaced by other additives in petrol. In order to see the effect this legislation the department of health (RIVM) started an investigation to the pollution of several forest soils located close to highways. The Dutch geological survey (now NITG-TNO) was asked to determine the natural background of lead and trace metals and to investigate the several sources of lead by means of Pb isotopes.

Material and methods

Two locations (Nunspeet and Moergestel) were selected from the existing monitoring network. These locations were sampled in 1990. To determine the influence of the change to unleaded petrol these two locations were samples again by NITG-TNO in 1997. From these locations topsoils and sediment (mostly driftsands with more than 90% quartz) were sampled at three distances from the highway. To get an indication of atmospheric deposition also some lichens were sampled at various distances from the highway in 1997. In addition, tree bark was sampled at Moergestel to investigate the accumulating effect of metals in plants.

Results

As expected, many trace metals increase closer to the highway. This effect is more prominent at the location Nunspeet than at Moergestel. Elements that show the largest enrichments are Pb, Zn and Cu. Other elements like Sn, Mo, Ag, As, Cr and *REE*'s increase as well. Almost all anthropogenic metal enrichments are found in the humic top soil. No enrichments are found below the humic layer. The concentration of the traffic related elements is strongly dependent on the amount of organic matter and the thickness of the humic layer. At location one (Nunspeet) the amount of organic matter is lower and the humic layer is thinner than at location 2 (Moergestel). This is also reflected in the amount of traffic related metals.

At both locations, lead and almost all other traffic related elements show a significant increase at both locations from 1991 to 1997. Lead isotopes at Nunspeet showed a shift for $^{206}Pb/^{207}Pb$ of 1.11 in

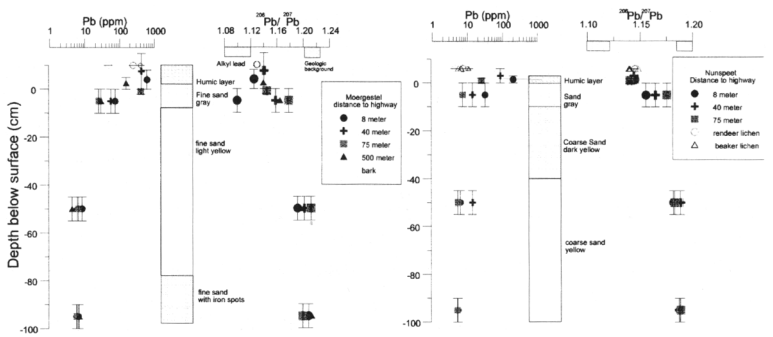

FIG. 1. Variation of Pb and Pb isotopes at Moergestel and Nunspeet at various distances from the highway.

TABLE 1. Increase of Pb and sources of Pb between 1991 and 1997 close to highways in the Netherlands

Location humic samples	Year	Lead concentration	$^{206}Pb/^{207}Pb$	Antropogenic contribution	Broken Hill petrol contribution	Other lead (%)
Nunspeet 8 m from A58	1991	118	1.121	2360%	79%	21
Nunspeet 8 m from A58	1997	199	1.145	3980%	24%	76
Index (1991 = 100)		+169				
Moergestel 10 m from A28	1991	341	1.114	6810%	92%	8
Moergestel 10 m from A28	1997	605	1.125	12100%	67%	33
Index (1991 = 100)		+178				
Nunspeet 75 m from A58	1991	35	1.130	700%	67%	33
Nunspeet 75 m from A58	1997	25	1.140	500%	49%	51
Index (1991 = 100)		+71				
Moergestel 75 m from A28	1991	200	1.144	4000%	26%	74
Moergestel 75 m from A28	1997	402	1.144	8040%	25%	75
Index (1991 = 100)		+201				

1991 towards 1.14 in 1997 in the humic layer. In Moergestel, the shift in Pb isotopes was similar to Nunspeet at the top of the humic layer, but disappeared lower in the soil profile (Fig. 1). The $^{206}Pb/^{207}Pb$ ratio of atmospheric deposition as measured in the lichens showed also a value of 1.14 in 1997 (Not measured in 1991). The sampled bark at Moergestel showed high concentrations of metals (Pb 300 ppm; Cu 40, Ni 10, Zn 80, Cd 1) relatively to the metal concentrations in the lichens and are also independent from the distance from the highway.

Discussion

The differences in the effect of highway between the two locations can be explained by a higher 'background' atmospheric contribution at the location Moergestel than at location Nunspeet. This is because Nunspeet is situated in a less populated area than Moergestel without major industrial activities. In addition the forest at Nunspeet is more dense and not interrupted by agricultural plots. Other factors that explain the differences between the two sites are the amount of traffic, the type of forest and the thickness and composition of the humic layer.

The amount of traffic at the Moergestel site is higher than at Nunspeet. Also, the forest is mostly planted with deciduous trees, in contrast with Nunspeet where pine trees are dominant. In addition, the humic layer is much thicker at Moergestel than at Nunspeet. This allows more metals to accumulate in Moergestel than in Nunspeet. In addition, the lower soil pH in Nunspeet due to pine needles, enhances the transfer of metals from the humic layer to the groundwater leading to lower concentrations. As indicated by the lead isotopes, all Pb that existed in the humic layer in 1991 is replaced in 1997 by lead with another $^{206}Pb/^{207}Pb$ ratio. Due to the high permeability of the soil, this lead has probably entered the groundwater system. This effect is less pronounced in Moergestel where, due to the thickness and composition of the humic layer, the transfer time to the groundwater is somewhat longer. The intermediate $^{206}Pb/^{207}Pb$ ratio of 1.13 in bark indicates that metal accumulation in trees is averaged over a 10 year period.

Conclusion

Despite the efforts to reduce traffic related emissions in the Netherlands these have increased almost two-fold in the last 6 years (table 1). Especially forest soils are prone to traffic related pollution. This is enhanced by the thickness and composition of a humic layer. A cause for the increase in pollution is the heavier traffic on the Dutch highways and an relative increase of other atmospheric sources. The shift in $206Pb/^{207}Pb$ from 1.11 in 1991 to 1.14 in 1997 shows that no more broken hill alkyl-lead petrol is being used in the Netherlands. This indicates that modern low lead petrol has a different isotopic signature.