FIELD DERIVED BCFs IN PINE NEEDLES FOR THE CALCULATION OF AIR CONCENTRATION OF DIOXINS

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Introduction

Vegetation was recently used as a monitoring tool to track the distribution of Persistent Organic Pollutants (POPs) in the troposphere (1,2,3,4). Pine needles, in particular, were analysed in a number of regional-size investigations of spatial trends of air concentrations, revealing concentration levels and "fingerprint" of a particular area (5,6,7). Needles are considered as passive samplers, being most of their retentive capacity due to their lipid-rich tissues. Laboratory approaches were developed (8,9) to correlate uptake with physico-chemical properties, such as octanol-air partition coefficient (Koa). More recent studies raised several issues concerning the meaning of pine needle concentration data and especially the variability in the uptake characteristics of different plant species with different compounds (10, 11). Dioxin content data in pine needles are scarce in the present literature. This paper is an attempt to explore the possibility of using pine needles as a tool for monitoring air contamination by dioxins and to tentatively backcalculate average air concentrations using pine needle data and empirically derived BCFs. In order to do so, long term air samples and pine needles were collected at different locations, both in rural and urban sites.

Materials and methods

Long term air sampling was carried out in three locations: Seveso (MI) ex zone A (Bosco delle querce), Milan (Via Eritrea) in a high traffic area and Cremona (average of three samplers). The air samplers were working for 15 minutes every two hours for a year (Nov. 1996 to Dec. 1997) for Milan and Seveso, while only for two weeks for Cremona (Apr.- Jul. 1997). Cremona location is a low population density urban site. The air samplers were made of a glass fibre filter followed by a prewashed polyurethane foam plug that was connected to a suction pump (12). Both airborne particles and vapour-phase PCDDs were collected. Before sampling the glass fibre filters were spiked with a mixture of 15 ^{13}C-labelled 2,3,7,8-substituited congeners to compensate the losses of the analytes during both the sampling and the entire analytical procedure. Pine needle samples were collected at 4 different locations (2 urban and 2 rural). Species sampled at each location are as follows: Milano (*Pinus strobus*), Seveso (*Pinus sylvestris*), Oga (*Pinus sylvestris*), Cinque terre (*Pinus pinaster*). The first two sampling site were adjacent to the air samplers and are characterised by industrial and urban sources. *Oga* is a mountain site (altitude of 1300 m a.s.l.) while *Cinque terre* is a coastal site on Ligure Sea., both located far from potential sources. The needles sampled were two years old and were located in the outmost branches, at a height of approximately 2 m. Samples were wrapped in aluminium foil, placed separately in polyethylene

bags and kept at a temperature of -20 °C until extraction. The air samplers (glass fibre filter and PUF) were soxhlet extracted with toluene (pesticide grade) and the extract purified by Extrelut columns coated with sulphuric acid, alumina column and finally activated carbon (12,13). Pine needles (about 200 g of dry needles) were spiked with 2.5 ng of a mixture of 15 ^{13}C-labelled 2,3,7,8-substituited congeners and soxhlet extracted for 24 h with n-hexane/acetone 9:1 (pesticide grade) and the extract purified by Extrelut columns coated with sulphuric acid, silicagel column and finally alumina column (13).
Instrumental analysis was carried out with a Dani 6500 - VG 70-250 HRGC-MS. The mass spectrometer resolution was 5000. Two capillary columns were used: a Chrompack CP-SIL 88, 50 m x 0.25 mm i.d., 0.25 µm film thickness and a SGE BPX 5, 50m x 0.2 mm i.d. x 0.25 µm film thickness. Dioxins were analysed as total isomers for each chlorinated class.

Results and discussion

Figure 1 shows the concentrations of total TCDD, PeCDD, HeCDD, HpCDD and OCDD (in this order for each sampling location) in pines from the different sampling sites (MI = Milano; SE= Seveso; OG = Oga; 5T= Cinque Terre) and reveals that pine needles are excellent samplers for dioxin contamination: concentrations are higher for urban sites while much lower (a factor of about 5 to 6) for rural locations. Levels in Seveso are approximately half way between those in Milan and in rural areas. Applying the fingerprint technique to these data and therefore expressing the relative ratio of total isomers as a percentage of the total dioxins (Figure 2) one can observe that fingerprints are quite different between the various locations, being the sites far from the sources dominated by the higher chlorinated compounds, probably indicating a limited presence of the lighter compounds, maybe due to atmospheric degradation of those chemicals.

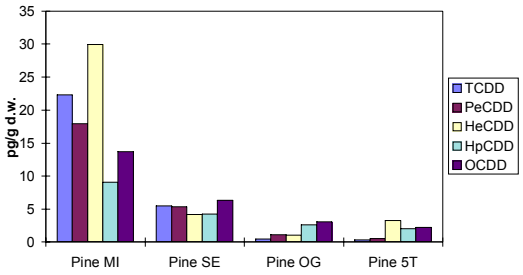

Fig. 1 Dioxin concentrations in pine needles

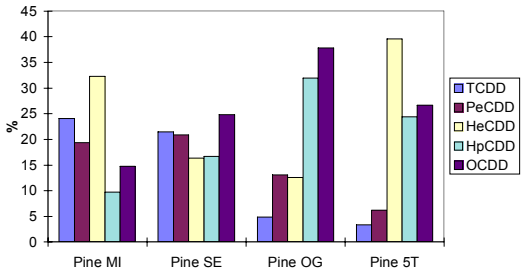

Fig. 2 Dioxin fingerprints in pine needles

Air concentration data from the three sampling stations are shown in Figure 3, depicting similar trends for the spectrum of congeners and concentrations, while the semi-urban Cremona station is characterised by lower levels. Concentrations were higher for the more chlorinated dioxins in all samples. A comparison of these results with the pine needle concentrations and fingerprints for the common sites (Milano and Seveso, Fig. 1 and 2) depicts a "sampling behaviour" of needles which favours less chlorinated dioxins in the uptake. This can be explained by the reduced availability of

highly chlorinated dioxins (probably associated with air particulate) and the slow kinetics of the uptake of such hydrophobic compounds.
Empirical BCFs were calculated for dioxins from pine needle and air concentrations in the two locations for which air and pine needle data were simultaneously available (Milan and Seveso). Their comparison (figure 4) shows that the log BCFs have similar trends but differ for a constant factor, which varies between 3 and 5 (BCF values). This might indicate an interspecific difference in dioxin uptake due to the different pine species. It also to be noted that the trend is inversely related to the trend of Koa which increases with the increased chlorination of dioxins, from log 9.67 for 2,3,7,8-TCDD to 11.76 for OCDD. Increasing concentrations in needles would instead be expected using Bacci's equation (9) to calculate the uptake from Koa. These results show that Bacci's equation should not be used to predict air concentration for this group of compounds.

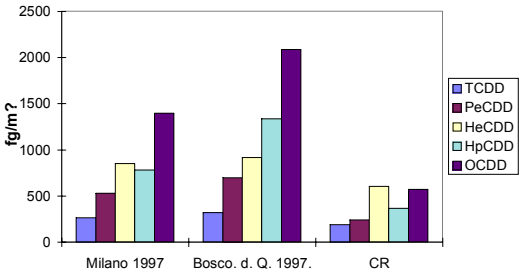

Fig. 3. Dioxin concentrations in bulk air

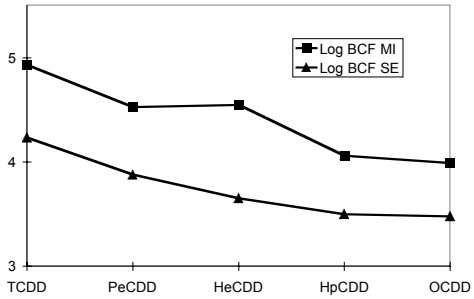

Fig. 4. Empirical Log BCFs for total dioxins

An initial attempt of backcalculating air concentrations for the Oga site from empirical BCFs has been made using the same field BCFs obtained for the Seveso site in figure 4. The Oga site was selected because pine needles belonged to the same species used for the calculation of BCF (*Pinus sylvestris* of Seveso site). The results are illustrated in Figure 5 and compared to the other air concentrations available, and reveal some similarities with less polluted sites. Such air concentration predictions are to be considered preliminary, especially because of the uncertainty related to the treatment of the dioxin uptake in needles as "total" of each class. The results of the prediction of the air concentrations at the Oga site reveal that the pattern (or fingerprint) of dioxins is characterised by the highly chlorinated compounds (HpCDD and OCDD), which are a factor of 4-50 higher than the other compounds.

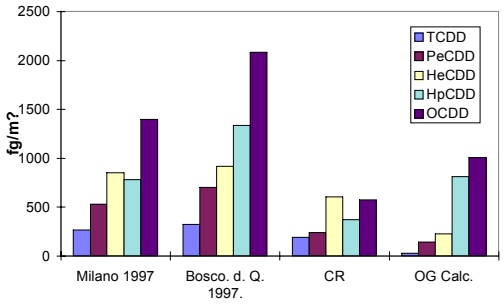

Fig. 5 Comparison of air concentrations: measured (see fig. 3) and calculated from empirically derived BCFs (OG Calc.).

The results show that pine needles can be employed as indicators for contamination by dioxins, both in terms of concentrations and fingerprint analysis. More specifically, fingerprint analysis and the comparison with long term measured air concentrations seems to show different patterns of uptake of dioxins in pine needles, in urban and rural sites. Some more work has to be done in order to clarify the reasons for the difference of air and pine needle fingerprint and to quantify the impact of the different factors involved in the accumulation process (species variability, degradation in air during transport, temperature) both in terms of pattern of isomers and congeners and concentrations. When the pattern and kinetics of uptake of dioxins in pine needles will be better defined, the use of pine needles (and possibly other vegetation types) would allow to better understand the spatial distribution of dioxins in the environment.

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