POLYCHLORINATED BIPHENYL, DIBENZODIOXIN, AND DIBENZOFURAN
OCCURRENCE IN THE GENERAL ENVIRONMENT IN ITALY

di Domenico A., Ferri F., Fulgenzi A.R., Iacovella N., La Rocca C., Miniero R., Rodriguez F., Scotto di Tella E., Silvestri S., Tafani P., Turrio Baldassarri L., Volpi F.
Laboratory of Comparative Toxicology and Ecotoxicology,
Istituto Superiore di Sanità, 00161 Rome, Italy

Polychlorinated biphenyls (PCBs), dibenzodioxins (PCDDs), and dibenzofurans (PCDFs) are widespread environmental micro-contaminants. Aside from PCBs which have been produced industrially, PCDD and PCDF occurrence is incidental and associated with natural causes and, indirectly, anthropogenic activities. Each family consists of a large number of analogs, several of which are very toxic; the toxic potential includes carcinogenicity at very low chronic exposures. Since available data indicate that PCBs, PCDDs, and PCDFs are present in the fat and blood of the general population, human exposure to such compounds is a matter of great concern. Therefore, detection in environmental matrices of the above chemicals and, specifically, of their toxic terms has great relevance to the assessment of man's health risks. On these premises, this laboratory has begun a monitoring program of the soil and sediment of the general environment aimed at assessing PCB, PCDD, and PCDF background levels and possibly their distribution pattern. The first outcomes of the investigation are reported here.

Sampling was carried out in five Italian regions (Fig. 1), at or slightly above sea level ("V" samples; Nos. 12-18, 21, 22, 25, 26), at an altitude of 800-1300 m ("P" samples; Nos. 1-7, 19, 20, 23, 24), and in caves normally not visited by the general public ("S" samples; Nos. 8-11, 27, 28). Sampling sites were chosen far away from cities, at least 5 km away from towns or villages, in unfarmed fields, and possibly in wild areas. Soil was collected by coring or trowelling the top layer to a depth ≤ 7 cm; moist or dry cave sediment was obtained by trowelling.[1,2] Weights of sample matrices after pretreatment[1,2] ranged from 1 to 3 kg. The analytical procedure, from the extraction step to HRGC-MS (MID) assessment, has been reported and evaluated elsewhere.[1-3] Here it suffices to say that all T_3CB to H_7CB homolog-specific determinations (N = 28 samples) were above detection threshold (DT); on the contrary, of the 27 (one missing) congener-specific assessments of PCDDs and PCDFs, expressed as "TCDD international equivalents",[4] the lowest three outcomes were below DT ($8.6 \cdot 10^{-2}$ ngTE/kg),
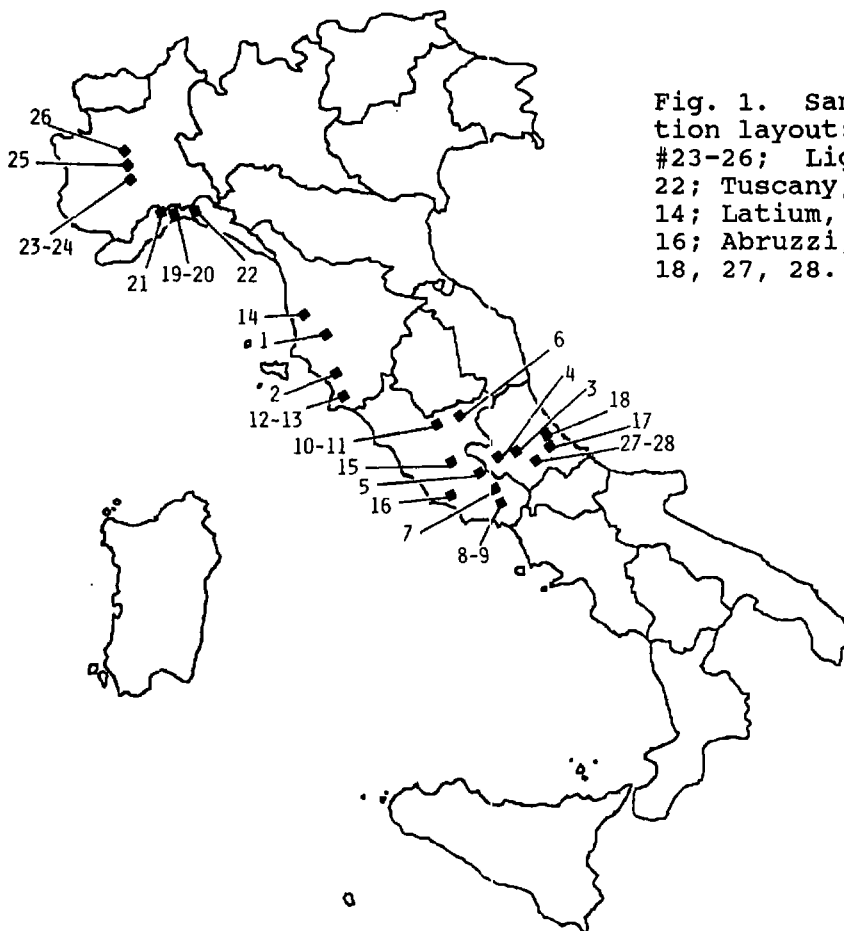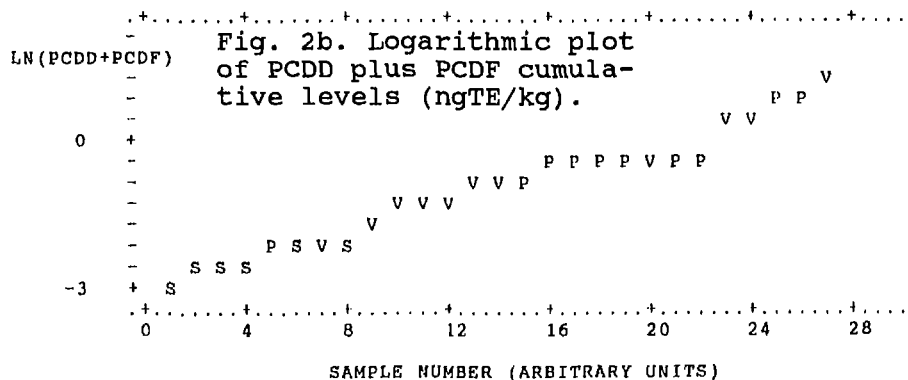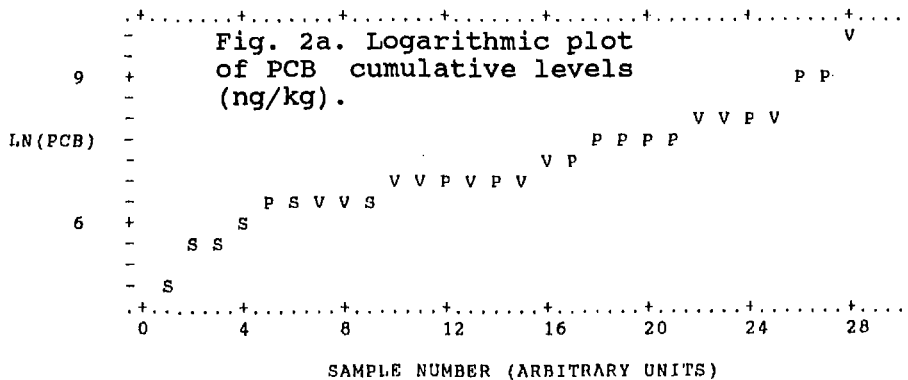
Fig. 1. Sampling location layout: Piedmont, #23-26; Liguria, #19-22; Tuscany, #1, 2, 12-14; Latium, #5-11, 15, 16; Abruzzi, #3, 4, 17, 18, 27, 28.

according to a study in preparation by Tafani et al.

The sets of ln-transformed levels of PCBs and PCDDs plus PCDFs were statistically analyzed; they are shown plotted separately (Fig. 2) after being independently ordered according to the increasing values within each set. Both sets, and their V-, P-, and S-sample subsets, have Gaussian distributions. PCB S-samples are concentrated in the lowest end of the pertinent distribution (Fig. 2a), between $1.1 \cdot 10^2$ and $6.8 \cdot 10^2$ ng/kg; the remaining PCB values, obtained from V- and P-samples, range from $6.2 \cdot 10^2$ to $1.6 \cdot 10^4$ ng/kg. Both the Student's t-test and Mann-Whitney test failed to prove that the mean and the distribution of the V-sample data are significantly different from those of the P-sample data; however, the mean and the distribution of the S-sample data make up a separate group with a high level of statistical significance (for both tests, $P < 0.001$).

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 .+.......+.......+.......+.......+.......+.......+.......+.....
       -       Fig. 2a. Logarithmic plot            V        -
    9  +        of PCB  cumulative levels        P P.         +
       -        (ng/kg).                     V V P V          -
LN(PCB)-                                  P P P P             -
       -                         V P                          -
       -             V V P V P V                              -
       -       P S V V S                                      -
    6  +     S                                                +
       -   S S                                                -
       -                                                      -
       - S                                                    -
 .+.......+.......+.......+.......+.......+.......+.......+.....
    0       4       8      12      16      20      24      28
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                    SAMPLE NUMBER (ARBITRARY UNITS)

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          .+.......+.......+.......+.......+.......+.......+.......+.....
              -        Fig. 2b. Logarithmic plot                     -
LN(PCDD+PCDF) -        of PCDD plus PCDF cumula-            V         -
              -        tive levels (ngTE/kg).          P P           -
              -                                     V V              -
           0  +                                                      +
              -                    P P P P V P P                     -
              -              V V P                                   -
              -        V V V                                         -
              -      V                                               -
              -   P S V S                                            -
              - S S S                                                -
          -3  + S                                                    +
          .+.......+.......+.......+.......+.......+.......+.......+.....
              0       4       8      12      16      20      24      28
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                    SAMPLE NUMBER (ARBITRARY UNITS)

For PCDDs and PCDFs (Fig. 2b), S-sample levels fall in the
range of $5.7 \cdot 10^{-2}$ to $1.2 \cdot 10^{-1}$ ngTE/kg, whereas the remaining V-
and P-sample data vary from $1.0 \cdot 10^{-1}$ to 4.3 ngTE/kg. Here,
again, the mean and the distribution of the S-sample data prove
to be significantly (for both tests, in all cases, $P < 0.005$)
different from the means and the distributions of V- and P-
sample data taken separately or together. The latter have
means ($4.6 \cdot 10^{-1}$ and $6.9 \cdot 10^{-1}$ ngTE/kg, respectively) which are
not statistically distinguishable; however, the Mann-Whitney
test did not provide strong evidence ($P < 0.11$) that the two
data sets belong to the same population. A correlation analy-
sis between PCDD plus PCDF TE values and the parallel PCB
values was also carried out (Fig. 3): in the logarithmic plane,
the linear regression proves to be highly significant. Revert-
ing to linear coordinates yields:

$$[PCDD+PCDF] = 8.90 \cdot 10^{-4} \cdot [PCB]^{0.853}$$

Based on this equation and the available data, the ratio
[PCDD+PCDF]/[PCB] is estimated to range from $2 \cdot 10^{-4}$ to $5 \cdot 10^{-4}$.

Fig. 3. Linear regression analysis of 24 PCDD plus PCDF and PCB pairs. Three data were excluded (below detection threshold) and one was missing in the PCDD plus PCDF set.
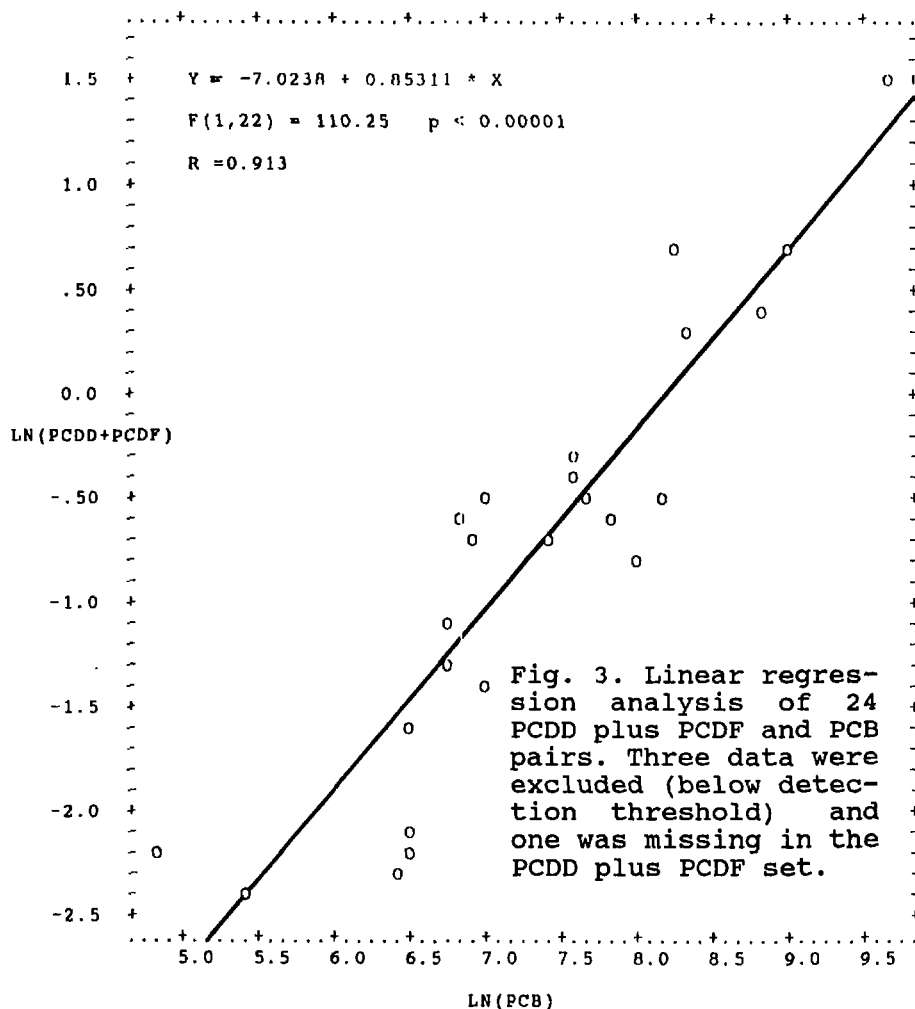
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