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COMPREHENSIVE ANALYSIS OF HEAVILY OCDD CONTAMINATED SOIL

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Introduction

The OCDD phenomena - specific PCDDs/Fs congener pattern characterized by an overwhelming dominance of OCDD with sharp decreases in the concentration of other PCDDs over the chlorination degree and vanishingly low levels of PCDFs had been found in soils and sediments from various parts of the world. Usually, this congeners profile detected in hot climate areas. Much more common is the strong dominance of OCDD in congener's profile. There are various assumptions about the phenomenon, but all of them could be refuted by evidence and but there is no reliable explanation for this phenomenon. In Vietnam, where we have been working for more than 20 years, OCDD dominates in almost all environmental and biological samples, but samples with nearly pure OCDD phenomena are rare. One sample was taken in 2005 in highlander area Sapa in north Vietnam. Later, we carried three expeditions to the detailed study of the territory. Such close attention caused by the unique location of this hot spot. It is a 2-3 square meter puddle on the edge of the flat top of the hill (the total area of about 50-100 m^2, the altitude of about 2200 meters) in unpopulated Hoang Lien national park. A few local residents use that area for pasture cattle and are wood harvesting that allegedly caused a strong forest fire about 15 years ago. This is a very wet country with very high levels of UV light and mild temperatures. In general, this area probably has the lowest level of dioxin contamination in Vietnam; OCDD concentration does not exceed a few tens of pg with congener distribution typical for pentachlorophenol (PCP). Elevated concentrations of OCDD were not found on top of the other hills and lowlands where rainwater accumulates. In 2010 on hot-spot we found fragments of the half-rotted plastic bag; same packages are widely used for the bulk of industrial products, including agrichemicals. This material was not very dirty by soil but contained same levels of OCDD and PCP/PCP salt (72.4 ng/g and 0.6 ng/g) as were found in contaminated puddle [1]. Unfortunately, we do not know when this piece of the bag got to the top and darkness has covered the questions who and why could bring chemicals, but we cannot exclude that it contained a substance that caused pollution. The last expedition took place in this area in 2011; then we dug a hole at the site of contamination. The results showed that contaminated only the upper layer.

Thus, summarizing all data about this point and in the region, we can completely exclude such reasons of OCDD anomalies, as any kinds of historical contamination or long-term accumulation of atmospheric deposition. Probably we are dealing with a modern source of contamination and some natural processes of transformation. In this case, we should found the precursors, metabolites or by-products, but their concentrations are too low for routine detection.

Materials and methods

Experiments were performed using a Finnigan MAT 95XP magnetic sector mass spectrometer with improved cooling system, reducing fluctuations and enhancing the accuracy of mass determination; mass chromatograms were recorded in the TIC and MID mode at resolution 8000-10000. The detailed method of detection and identification of unknown polychlorinated substances we published before [3,4].

In the text prefixes ortho-, meta-, and para- are used to indicate the position of methoxy group with respect to the Ar-O-Ar bond, disregarding other substituents. Relative concentrations were estimated as the ratio of abundance of monoisotopic molecular ions (sum of all isotopes) of the analyte to that of OCDD.

Results and discussion

The most obvious substances that associated with PCP and OCDD are polychlorinated biphenyl ethers and phenoxyphenols; molecular ions of the last one we found in before [2], but later were found that it is interference from other compound fragment ions. In this paper, we paid special attention to the identification reliability. Some mass spectra of relative compounds in database and retention time values do not guarantee the correctness of complex organic compounds identification. In this work, we haven't preliminary information for most compounds, and, probably, they were found for the first time. For identification of the individual compound or a group of isomers to which it may belong we use both facts and assumptions with following basic principles:

— sorting of possible element formulas for exact mass of molecular and fragment ions to select a most suitable, for this a special method was developed to elevate an effective resolving power to 50000-60000;

— matching of the distribution of intensities of four to five peaks, corresponding to different combinations of atoms ^{35}Cl and ^{37}Cl in the isotopic clusters in molecular and fragment ions, to the theoretical values;

— characteristic fragmentation patterns observed under electron ionization with the presence of at least four isotopic clusters of fragment ions, corresponding to the elimination of neutral species CH_3, CH_3CO, CH_3O, and Cl and their combinations;

— the absence of ions in the mass spectrum that could not form from the anticipated substance;

— cleavage of the Ar-O-Ar bond in diphenyl ethers; such decay is minor in character, but if it could be detected, the distribution of chlorine atoms and methoxy groups between aromatic rings could be determined.

— the presence of a methoxy group in the ortho position of the mono-MeO-PCDE is indicated by an intense ion peak corresponding to the elimination of CH_3Cl with cyclization into $[PCDD]^+$, that is confirmed by the corresponding fragmentation;

— di-MeO-PCDE with methoxy groups in ortho positions of both benzene rings, are characterized by an intense signal of ion cluster corresponding to cyclization into $[PCDD]^+$ with the same degree of chlorination and a less intense signal of an ion cluster corresponding to cyclization into $[MeO\text{-}PCDD]^+$;

— if only one of the two methoxy groups was in the ortho position or both of them were in the ortho positions of one ring, the ion cluster formed corresponded to $[MeO\text{-}PCDD]^+$.

Up to now 28 compounds were found, 24 of which were classified as methoxy-substituted polychlorinated dibenzo-p-dioxins (MeO-PCDD) and methoxy-substituted polychlorinated diphenyl ethers (MeO-PCBE) (Fig 1a,b). In several cases, we were able to find the exact structure, in other belonging to one of the isomers; some cases are necessary for extra proofs (marked italics in the figs). Some compounds we could not name, they could contain more carbon and hydrogen atoms; the presence of sulfur or bromine could not be excluded as well.

Three ring compounds were not found yet, but we cannot completely exclude their presence in the sample. Polychlorinated phenoxy phenols and methoxy-substituted PCDF were not detected at detection limit around 1 pg/g.

If we consider only the list of detected substances, it is possible to suggest that all of them, including OCDD, are products of some mysterious biological process, but this statement is too revolutionary that considered a true.

Another convenient theory is biotransformation of the organochlorinated compound, many of discovered compounds couldn't be considered metabolites of OCDD, but all of them can derive from PCP by the reactions, which are not contrary to common sense. The main problem with this model is the lack of significant amounts of PCP or its main metabolite - pentachloroanisole (~680 ppm from OCDD) in the sample; such levels of PCP and pentachloroanisole we can consider as the residual amount of the primary pollution or products of an unknown reaction. The second question is the fate of PCDF. We can remove both questions only if assume that a natural conversion process of pentachlorophenol salt to OCDD existing; i.e. the primary source was a small amount of PCP-Na accidentally brought by local residents. But again, this is radical proposal too.

So we came up with a method of ultra-trace detection and identification of unknown chlorinated substances; found two dozen compounds which in the literature considered as metabolites of PCDD and PCDE, but it is likely we are the first who found them in the environmental sample. However, we almost did not come close to solving the OCDD phenomena.

Acknowledgements

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References

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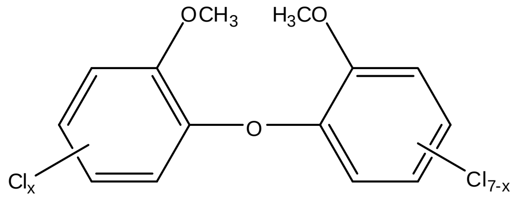
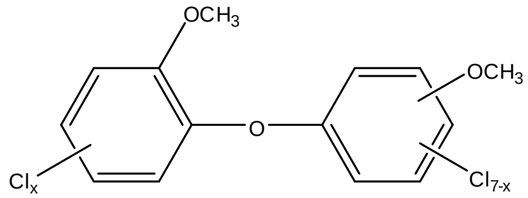
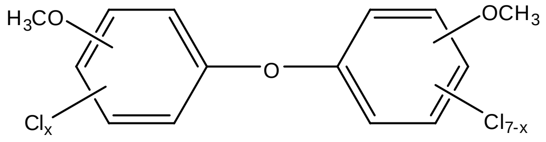


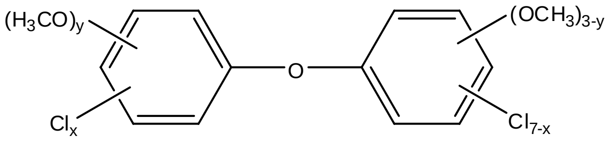
di-MeO-HpCBE
P7 - 20 ppm and P8 - 9 ppm



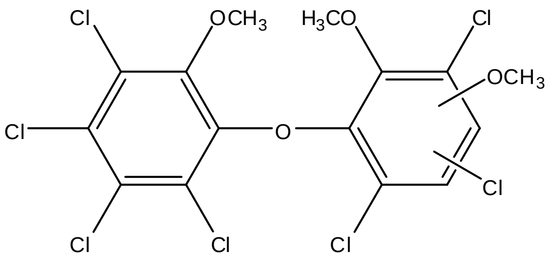
di-MeO-HpCBE
P9 - 4ppm and P10- 6 ppm



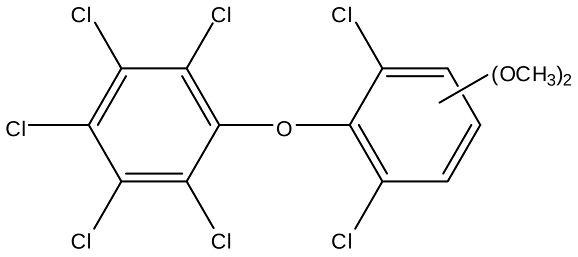
di-MeO-HpCBE
P13 - 4ppm and P14(non ortho)- 6ppm



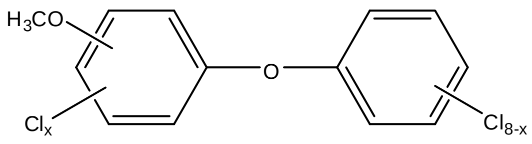
tri-MeO-HpCBE
P16 - 8ppm and P17- 4ppm



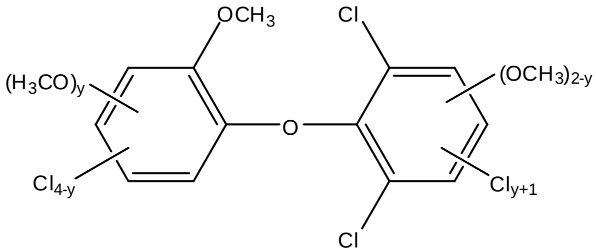
tri-MeO-HpCBE
XIV - 106ppm



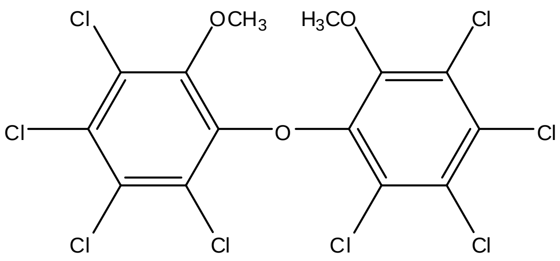
di-MeO-HpCBE (*)
XVI - 1626 ppm



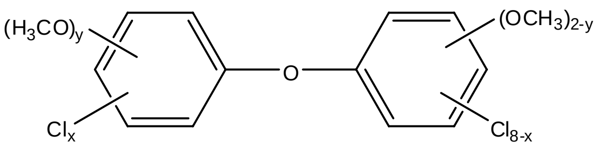
MeO-OCBE
P15 - 190 ppm



tri-MeO-HpCBE (y = 0 or 1)
F2 - 5614 ppm

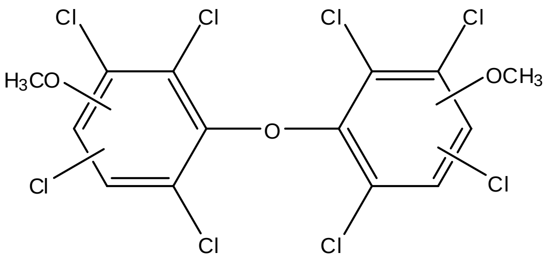


2,2'-di-MeO-OCBE
XVI - 2757 ppm

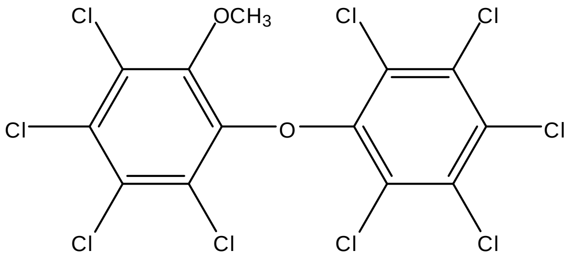


di-MeO-OCBE
P12(mono ortho) - 34ppm and P18 - 43ppm

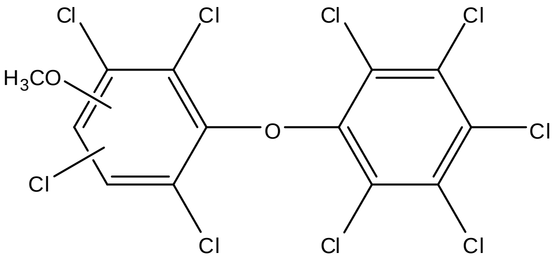
Fig. 1a. Substances founded in the soil with high concentration of OCDD and their ID code and concentration (relatively OCDD).
(*) - more probable structure



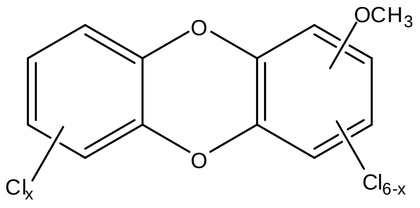
di-MeO-OCBE
II - 2631 ppm



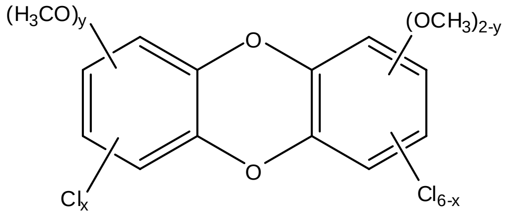
2-MeO-NoCBE
XVIII - 4 ppm



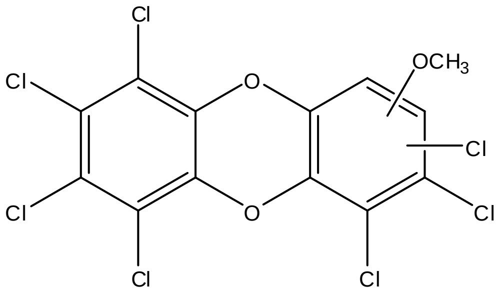
MeO-NoCBE (non ortho)
P1 - 1 ppm



MeO-HxCDD
P19 - 13 ppm



di-MeO-HxCDD
P22 - 4 ppm, P20 - 79 ppm, P21 - 27 ppm



MeO-HpCDD
XIX - 927 ppm and XX - 4406 ppm

Fig. 1b. Substances founded in the soil with high concentration of OCDD and their concentration (relatively OCDD)