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# The trans-continental distributions of pentachlorophenol and pentachloroanisole in pine needles indicate separate origins<sup>☆</sup>



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## ABSTRACT

The production and use of pentachlorophenol (PCP) was recently prohibited/restricted by the Stockholm Convention on persistent organic pollutants (POPs), but environmental data are few and of varying quality. We here present the first extensive dataset of the continent-wide (Eurasia and Canada) occurrence of PCP and its methylation product pentachloroanisole (PCA) in the environment, specifically in pine needles. The highest concentrations of PCP were found close to expected point sources, while PCA chiefly shows a northern and/or coastal distribution not correlating with PCP distribution. Although long-range transport and environmental methylation of PCP or formation from other precursors cannot be excluded, the distribution patterns suggest that such processes may not be the only source of PCA to remote regions and unknown sources should be sought. We suggest that natural sources, e.g., chlorination of organic matter in Boreal forest soils enhanced by chloride deposition from marine sources, should be investigated as a possible partial explanation of the observed distributions. The results show that neither PCA nor total PCP ( $\Sigma\text{PCP} = \text{PCP} + \text{PCA}$ ) should be used to approximate the concentrations of PCP; PCP and PCA must be determined and quantified separately to understand their occurrence and fate in the environment. The background work shows that the accumulation of airborne POPs in plants is a complex process. The variations in life cycles and physiological adaptations have to be taken into account when using plants to evaluate the concentrations of POPs in remote areas.

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## 1. Introduction

Since the 1960s, the awareness of problems caused by persistent organic pollutants (POPs), including trans-boundary and global issues, has grown. To address such issues, the Stockholm Convention (SC) on Persistent Organic Pollutants was developed (Stockholm Convention, 2016), calling signatory countries to develop legislation to reduce the risks posed by these compounds. The SC came into effect on 17 May 2004, and includes a mechanism to add new

compounds to the Convention. Pentachlorophenol (PCP) was added in 2015 with a few specified uses remaining legal (UNEP, 2015).

A complicating factor for the inclusion of PCP in the SC, is the scarcity of measurements of PCP itself in the environment (UNEP, 2013a, 2013b). This is largely due to the extra work required to determine an ionizable compound, such as a phenol, together with the traditional POPs, most of which are neutral. A seemingly convenient solution has been to use pentachloroanisole (PCA) as a proxy for PCP. PCA is formed in the environment by microbial methylation of PCP (UNEP, 2013a, 2013b); it is neutral and can easily be determined together with other POPs using standard protocols. Lacking known anthropogenic sources, it is generally presumed that microbial methylation of anthropogenic PCP is the only source of PCA in the environment (UNEP, 2013a, 2013b). Indeed, it was recently suggested that environmental authorities

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include PCA as a proxy for PCP in their monitoring programmes; PCP itself is not suggested (Palm Cousins et al., 2012). Other anthropogenic compounds, such as polychlorinated biphenyls, hexachlorobenzene, hexachlorocyclohexanes, and pentachloronitrobenzene, are discussed as possible precursors, but the formation of PCA from these precursors would proceed via PCP (UNEP, 2013a, 2013b).

Adding to the complexity, PCA has sometimes been quantified alone with no attempt to determine native PCP, but often PCP has been derivatized to PCA prior to determination to yield a measure of “total PCP” ( $\Sigma\text{PCP} = \text{PCA} + \text{PCP}$ ). Most published data on the environmental occurrence of PCP are, for this or other reasons, difficult to interpret (UNEP, 2013a, 2013b).

Because of the use of PCA or  $\Sigma\text{PCP}$  as proxy for PCP, the global distribution of PCP/PCA is presently difficult to assess. Ballschmiter and co-workers suggested that some chlorinated phenols and anisoles in the marine environment are of natural origin (Ballschmiter, 2003; Führer et al., 1997; Schreitmüller and Ballschmiter, 1996; Walter and Ballschmiter, 1991). However, for PCP/PCA they suggest strictly anthropogenic origins.

Regarding the global distribution, Simonich and Hites (1995), analyzing “tree bark”, claim to show that the environmental concentrations of PCA increase with latitude due to long-range transport and global distillation/fractionation processes as suggested by Wania and Mackay (1993). However, due to methodological ambiguities, we posit that alternative interpretations and additional considerations provide sounder explanations of the data presented. If variations in tree ecophysiology and bark chemistry are taken into account, the most likely interpretation of the Simonich and Hites (1995) material is that it reflects latitudinal differences in the gymnosperm/angiosperm ratio.

Other publications also indicate a northward concentration increase of  $\Sigma\text{PCP}$  both in Canada (Cessna et al., 1997) and in Europe (Eriksson et al., 1989; Jensen et al., 1992; Kylin, 1996; Strachan et al., 1994). Unfortunately, these studies either made use of too few samples to draw any specific conclusions (Cessna et al., 1997), and/or reported  $\Sigma\text{PCP}$  only (Cessna et al., 1997; Eriksson et al., 1989; Jensen et al., 1992; Kylin, 1996; Strachan et al., 1994), masking information critical for proper data interpretation. Most of these data were produced 1985–1996 within a collaborative project chiefly involving the authors of this paper (Eriksson et al., 1989; Jensen et al., 1992; Kylin, 1996; Strachan et al., 1994). Within that project, pine needles were used to map the distribution of airborne POPs, but the distribution of  $\Sigma\text{PCP}$  was difficult to understand in relation to known PCP use. We, therefore, undertook this expanded study to investigate if  $\Sigma\text{PCP}$  is a relevant environmental parameter, if PCA and/or  $\Sigma\text{PCP}$  are good proxies for PCP, and to obtain a better picture of the continent-wide distribution of these compounds.

## 2. Materials and methods

### 2.1. Sampling and samples

In Eurasia, sampling concentrated on Scots pine (*Pinus sylvestris* L.). This species has a wide distribution in Eurasia; it is also widely cultivated in areas where it is not native (Eckenwalder, 2009). However, in some cases where Scots pine was not available at a specific site, other species were sampled. In cases where samples were not collected by ourselves, in, e.g., Britain, the Balkans, around the Black Sea, and in Russia, the species collected were determined by a local botanist. For some samples, uncertainties as to species determination remain as indicated in the Supplemental data, Table S1. In other parts of the world, the sampled species are often unknown although it was always of the genus *Pinus*. A full list of all samples from different parts of the world is given in the

Supplemental data, Tables S1–S5.

Samples were collected during several field trips 1985–1996. For detailed sampling procedures, refer to previous publications (Jensen et al., 1992; Strachan et al., 1994; Kylin et al., 1996). In short, samples were taken at the southwest facing edge of a forest or from the south-western side of freestanding trees, preferably with >100 m of open ground to the southwest. Approximately 65% of all data included in this study are from samples collected by ourselves; remaining samples were collected by contacts at universities and science academies in the respective country and sent to us with express delivery. All available needle year-classes were analyzed separately.

### 2.2. Chemicals

Standards of PCP and PCA (99.9%), and pesticide grade dichloromethane (DCM), hexane, and acetonitrile (ACN) were from Kebo ([currently VWR] Spånga, Sweden). Radiolabelled pentachlorophenol- $^{14}\text{C}$ (U), specific activity 1.14 mCi/mM [4.32  $\mu\text{Ci}/\text{mg}$ ] was a gift from Ulf Ahlborg at the Karolinska Institute, while 4-Bromo-2,3,5,6-tetrachlorophenol (TCBP), was synthesized in house (Strachan et al., 1994). Analytical grade sulphuric acid, hydrochloric acid (HCl) and silica gel 60 were from Kebo, while analytical grade sodium hydroxide (NaOH) was from Eka-Nobel (Stenungsund, Sweden). Deionized water was produced in an Elgastat (Elga Ltd, High Wycombe, Bucks., England) with two extra carbon cartridges added to remove organics. Diazomethane was produced from diazald (Sigma-Aldrich, Haninge, Sweden) according to Sigma (2016). 4-Bromo-2,3,5,6-tetrachloroanisole (TCBA) and radiolabelled PCA and were produced by derivatizing TCBP or radiolabelled PCP with diazomethane.

### 2.3. Sample extraction and clean up

All glassware was cleaned by washing with ethanol and acetone, and heated at 300 °C for 24 h.

At arrival to the lab, whole, fresh needles were divided into year-classes, cut in pieces (~3 mm) and stored under dichloromethane (DCM) in test tubes with PTFE-lined screwcaps in a freezer (−20 °C) until extraction could be performed. When a high number of samples arrived at the lab simultaneously, the last samples of the consignment were typically extracted within a month. The samples were exhaustively extracted with DCM either in a Soxhlet apparatus (the Canadian lab) or in a specially designed extractor (Kylin et al., 1996). Before extraction, the surrogate standards TCBP and TCBA were added. The extracts were stored in sealed glass ampoules in a freezer (−20 °C) until analyzed. During methods development, the completeness of extraction had been checked by subjecting the DCM-extracted samples to a prolonged extraction of the residue with a solvent mixture with higher boiling point (chloroform:acetone, 1:1 vol:vol). These tests indicated that <1% of the analytes were left in the sample matrix after DCM extraction.

The extracts were transferred from the ampoules to test tubes with PTFE-lined screw caps, and the DCM volume was adjusted (2 mL). The acidic compounds were extracted into an aqueous phase containing NaOH (2 mL, 0.1 mol/L). When shaking, a slurry was formed as the long-chain carboxylates from the epicuticular wax will not dissolve fully in the alkaline aqueous phase. Full phase separation was accomplished by centrifugation (1500 rpm, 1 min) in a benchtop centrifuge, after which the DCM phase was transferred to another test tube. To the test tube with the aqueous phase, new DCM (2 mL) was added and the aqueous phase was acidified with HCl (0.1 mL, 1.1 mol/L), the test tube was sealed and shaken until both phases were clear. The aqueous phase was again made basic with NaOH (0.1 mL, 1.2 mol/L), and the extraction procedure

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