Towards a global historical emission inventory for selected PCB congeners – a mass balance approach

3. An update.

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Abstract

Previously published estimates of the global production, consumption and atmospheric emissions of 22 individual PCB congeners (Breivik et al. 2002a,b) have provided useful information for later studies attempting to interpret contaminant levels in remote areas as well as in the global environment. As a result of the need for more contemporary emission data (following the year 2000), an update of this emission database is presented. This exercise takes into account new information on PCB production in Poland, as well as new data on the chemical composition of various technical mixtures for which less information had been available. The methodology to estimate temporal trends of PCB emissions associated with various types of PCB usage is improved. Projected emissions up to year 2100 are presented to facilitate predictions of future environmental exposure. The national emission data for each of the 114 countries considered is spatially resolved on a 1° x 1° grid for each congener and year, using population density as a surrogate.

Key words: PCBs; global; production; emissions; historical; scenarios

1 Introduction

Polychlorinated biphenyls (PCBs) are among the Persistent Organic Pollutants (POPs) that have been of most interest and concern (e.g. AMAP, 2004). International agreements are now coming into force to reduce the environmental exposure to POPs in remote areas because of their toxicities, persistence, bio-accumulative properties and long-range atmospheric transport (LRT) features (UN/ECE, 1979/1998; UNEP, 2001). In order to understand and predict the LRT features and environmental fates of these substances, quantitative information on their atmospheric releases is deemed essential (e.g. Breivik et al. 2004; Hung et al. 2005). Furthermore, emission inventories are also essential for identifying, evaluating and prioritising sensible control strategies on a regional or global scale (UN/ECE, 1979/1998; UNEP, 2001). The complementary uses of emission inventories by scientists and decision makers (Breivik et al. 2006) has resulted in some emission inventories mainly being targeted and/or used for research (e.g. for deriving source-receptor relationships on a regional or global scale) by emphasising completeness in terms of temporal, spatial and isomeric/congeneric coverage (e.g. Li et al. 2002/2003; Breivik et al. 2002b; Prevedouros et al. 2004), whereas other emission inventories are being developed and maintained by national agencies mainly for more direct policy-oriented use, thus containing more detailed information on emissions from specific sources and source categories (e.g. Vestreng et al. 2005).

POPs and POP-like chemicals may, from a simplified source perspective, be divided into two main classes; intentionally produced chemicals (various organochlorine pesticides as well as industrial chemicals like PCBs) and accidental by-products of various combustion processes (such as dioxins and polycyclic aromatic hydrocarbons). Existing emission inventory methodologies and reporting formats as developed for the classical air pollutants (e.g. SO_2,

NO_x) are therefore considered suitable and relatively easy to adapt for the accidental by-products (EEA, 2005; UNEP, 2005). Nationally reported data on emissions of PAHs and PCDD/Fs are therefore also available from several countries (Vestreng et al. 2005), with complementary studies presented in the scientific literature (e.g. Pacyna et al. 2003; Quass et al. 2004; Xu et al. 2006). However, this classical emission factor approach (whereby statistical activity data are multiplied by appropriate emission factors) is considered less suitable for intentionally produced chemicals. In order to quantify atmospheric emissions of chemicals that are intentionally produced, consideration must therefore be given to the possibility that emissions could occur during the entire lifecycle of such chemicals (e.g. production, storage, use and disposal). While there has been some progress in understanding the sources and emissions of certain OC pesticides on a regional (e.g. Breivik et al. 1999; Li et al. 2001/2004/2006) and global scale (e.g. Voldner and Li, 1993; Li et al. 2000/2003), information on emissions of industrial chemicals remains fragmented in comparison because of empirical limitations and methodological difficulties (Prevedouros et al. 2004a; Breivik et al. 2002b; Denier van der Gon et al. 2005). This may in part be attributed to the fact that control strategies governing intentionally produced chemicals are mainly targeted towards safe collection and destruction of products and waste containing harmful chemicals like PCBs, rather than evaluated on the basis of variable emission strengths during the lifecycle of these chemicals (note that this approach does not necessarily discriminate between sources with a high and low potential for environmental releases). As a result, most emission inventories for intentionally produced chemicals seem to be motivated by research needs, thus aiming to support environmental fate studies.

The methods, results and uncertainties of the effort to quantify the global production, consumption and emissions of PCBs globally have been described in detail previously (Breivik et al. 2002a,b). The current study extend this work to present an update of this dynamic mass balance approach to further facilitate studies using the PCB data in the context of environmental fate studies, mass balance studies and for the interpretation of monitoring data. A specific focus has been on improvement and discussion of the methodological approach used for estimating temporal trends. This was deemed essential, as PCBs are still omnipresent in the global environment, despite the bans on PCB production in developed countries that entered into force more than three decades ago. Finally, we have also included scenarios for how the emissions of PCBs may possibly develop until year 2100, thus allowing for consecutive studies on the overall global fate of PCBs from cradle to grave. Atmospheric emissions of PCBs caused by de novo synthesis are not considered in this inventory, as they are not believed to contribute significantly to the overall global historical mass balance for PCBs (Breivik et al. 2002b). This is in accordance with studies by other groups who suggest that intentionally produced technical mixtures of PCBs are the main source, even of dioxin-like PCBs, into the environment (Tanabe et al. 1987; Takasuga et al. 2006)

2 Methods

2.1 Production and consumption

A detailed description of the methodology used to estimate the global production and consumption of PCBs is discussed in Breivik et al. (2002a). In brief, available data on the temporal trend in production of total PCBs, technical PCB mixtures and the chemical composition of various technical PCB mixtures was compiled from the literature. For some producers with less detailed information, the production of individual PCB constituents was estimated, in order to present an estimate for individual homologues and selected congeners on a global scale, along with a simplified estimate of uncertainties contained in these estimates. Data on temporal trends in PCB import/export within various countries and regions was also compiled, together with national PCB usage data, to reach an estimate of the temporal trend in the global consumption pattern for 114 different countries world-wide.

2.2 Emissions

A simple dynamic mass balance model was developed (Breivik et al. 2002b) in an attempt to bridge consumption and consecutive emissions of 22 individual PCB congeners, caused by PCB usage (open usage, small capacitors, nominally closed systems and closed systems), accidental releases (spills to soil, fires) and the disposal of products containing PCBs (landfills, open burning, waste incineration and destruction). The model was parameterised on the basis of the limited empirical quantitative understanding of various atmospheric loss processes. To illustrate and highlight some of the resulting uncertainties, three different emissions (max, default, min) estimates were therefore presented and discussed by Breivik et al. (2002b).

The original model has been used and applied in this study, with one important modification. In the former study, each PCB usage category was assigned a fixed average product lifetime. These four average lifetimes (k_a) ranged from 5 years (open usage) up to 25 years for closed systems (large capacitors and transformers) under the default scenario. Throughout the time period for which the PCBs are in use, losses occur due to atmospheric emissions and potential accidental releases. By the time the product has reached its use-life expectancy (assumed equal to the average lifetime), the remaining PCBs (not subject to losses during use) were disposed (Breivik et al. 2002b). A limitation with this approach is the assumption that no products containing PCBs are disposed prior – or after – the products use-life expectancy. This limitation was overcome here by modelling use-life expectancies of each usage category as a temporal distribution. This was deemed essential for improving the predicted temporal trend in emissions from usage, particularly reflecting the current post production period (i.e.

for the time-period when most PCBs in use would be about to be disposed, according to the old methodology and the use-life expectancies applied).

Specifically, the use-life expectancies of each usage category were assumed to follow the so-called "bathtub" curve (Fig 1A) which is a simplified approach used in reliability engineering to predict the overall failure rate of a product during its lifecycle (e.g. Pecht et al.1994; Blanks et al. 1998; Pecht et al. 2002, Linton et al. 2004). The total failure rate and hence the amount of PCBs disposed at any time is determined by three individual failure rate curves determining t; (a) random failure (i.e. a constant failure rate), (b) infant mortality (i.e. an exponential decline to take into account enhanced early failures), and (c) wear-out (which is modelled as an exponential increase in failure rates). It was also assumed that the initial and final failure rate due to mortality and wear-out was three times higher than the random failure rate, respectively. The sum of these failure rates was scaled to yield unity, implying that all PCBs introduced in a given year are disposed of by the time when twice the use-life expectancy has passed. The result of this approach is exemplified in Fig 1B for a given amount of specific PCB congener, assigned to a particular usage category in year 1 (scaled to 100%) with a use-life expectancy of 15 years. The amount remaining in use in this example shows an approximate exponential decline during the first 15 years, and then a more or less linear decrease afterwards. The temporal trend in losses due to disposal and emissions during use are depicted on the 2nd y-axis (Fig 1B). Whereas the temporal trend in emissions would be a mirror image of the trend in usage, albeit on a different scale (Fig 1B), the temporal trend in disposal would reflect both the temporal trend in the overall failure rate (Fig 1A) and the amounts left in use at any time. Thus, if the specific emission factor has a low value, the trend in disposal would follow the temporal trend in the overall failure rate. However, if emission to air is a significant loss process (i.e. high emission factor), then the amounts finally disposed towards the end of the time-period would be less than the amounts disposed at the beginning (Fig 1B).

2.3 Spatial distribution

The PCBs have a usage profile in various countries that is intimately linked with various anthropogenic activities (Breivik et al. 2002a), and several monitoring studies have clearly shown that the atmospheric levels of PCBs tend to have an elevated "urban" signal in comparison to many other POPs (e.g. Hafner and Hites, 2003; Harner et al., 2004; Jaward et al., 2004a). For these reasons, population density is considered a suitable surrogate for spatial distribution of national emissions within each of the 114 countries that are explicitly considered in the inventory (Breivik et al. 2002b), and for this purpose we used the 1º x 1º global population density database (Dr.Yi-Fan Li, Environment Canada).

3 Results

3.1 Production and consumption

3.1.1 Total PCBs

The compiled data on historical production of total PCBs by factory are presented in Table 1. These data are similar to the data presented by Breivik et al. (2002a), except that quantitative information on PCB production in Poland has now become available (Falandysz, 2000; Zułkowski et al. 2003). PCBs were produced at two different factories in Poland. An estimated amount of 1000 tonnes of a technical PCB mixture called "Chlorofen" was produced by Electrochemical Company in Zabkowice between 1966 and 1970 (Zułkowski et al. 2003). In addition, 679 tonnes of a technical mixture named "Tarnol" was later produced by Zaklady Azotowe between 1974 and 1977 (Falandysz, 2000; Zułkowski et al. 2003). We previously claimed that production of PCBs had also occurred in East Germany and Austria in addition to Poland (Breivik et al. 2002a and references therein). On basis of this information, a consultation of experts was carried out in Austria with the result that PCBs were never produced in Austria (Weiss P., personal communication).

3.1.2 Production of individual homologues and congeners

The homologue and congener content of each specific technical mixture tends to vary from batch to batch (e.g. de Voogt and Brinkman, 1989; Kodavanti et al. 2001) and between different analytical determinations (e.g. Frame, 1997). The composition of the highly chlorinated Chlorofen mixture was initially determined by Falandysz et al. (1992), and has later been evaluated in a several consecutive studies (e.g. Falandysz et al. 2004; Ishikawa et al. 2005). In order to estimate the homologue production due to the production of Chlorofen, we used the average homologue content from three independent studies (Falandysz et al. 1992; Ishikawa et al. 2005; Takasuga et al. 2006), whilst the congener content was based on the average results from studies by Falandysz et al. (1992), Takasuga et al. (2006) and Wyrzykowska et al. (2006). The maximum and minimum values of the reported homologue and congener content of Chlorofen were used to estimate the associated uncertainty of the results (see also Breivik et al. 2002a). Less information seems to be available with respect to the chemical composition of “Tarnol”, but two studies report that it has a similar chemical composition as Aroclor 1248 (Falandysz, 2000; Zułkowski et al. 2003). Thus, we have used the compositional data on Aroclor 1248 as previously compiled (Breivik et al. 2002a) in order to estimate the homologue and congener content of Tarnol.

This update also allowed us to take into account new information on the chemical composition of the technical mixtures that were produced in the former Czechoslovakia (Delor). According to Schlosserová (1994), 14,140 tonnes was produced as Delor 103, 4,381 tonnes was produced as Delor 106 and 2,961 tonnes was produced as other PCB mixtures.

The homologue and congener production of Delors 103 and 106 was estimated based on information from de Voogt and Brinkman (1989), Taniyasu et al. (2003) and Wyrzokowska et al. (2006), whilst the uncertainty was estimated in a similar fashion as described for Chlorofen. The remaining PCB production was attributed as an equal mixture of Delors 104 and 105 with a chemical composition as reported by Taniyasu et al. (2003), using the max/min values of the composition of these mixtures as an estimate of the upper and lower boundaries of homologue and congener production. Likewise, we were also able to include information on the production of the selected constituents of Aroclor 1268 (Kannan et al. 1997; Ishikawa et al. 2005; Wyrzykowska et al. 2006), which were missing in the former study (Breivik et al. 2002a).

The updated estimate for the cumulative global production of individual homologues and congeners, along with the estimated uncertainties, is presented in Figure 2. These results are almost identical to the results presented in Breivik et al. (2002a), except that this estimate is somewhat higher for more chlorinated homologues (deca-CB in particular), mainly as a result of taking into account the new information on Aroclor 1268. Of the 1,325.81 kt of technical mixtures of PCBs that has been produced, the results suggests that 27.7 % were produced as tri-CBs (367.3 kt; range 330.1 kt - 421.4 kt), 25.3% as tetra-CBs (334.6; 313.2–359.8 kt), 19.5% as penta-CBs (257.9; 216.7–285.2 kt), 11.3% as hexa-CBs (150.3; 118.1-173.5 kt), 9.6% as di-CBs (126.8; 108.7-155.2 kt), 4.7% as hepta-CBs (62.7; 46.5-79.8 kt), 1.2% as octa-CBs (15.8; 10.9-21.2 kt), 0.5% as mono-CBs (6.8; 4.2-10.3 kt), 0.2% as nona-CBs (2.6; 1.5-4.0 kt) and 0.02% as deca-CB (0.2; 0.07-0.4 kt). The production of the 22 selected PCB congeners (Fig 2B) accounts for 565.36 kt (467.31-702.38 kt) or 42.6% (35.3%-53.0%) of the historical production. Likewise, the production of seven frequently reported PCBs (PCB-28,52,101,118,138,153 and 180) accounts for 17.8% (14.7%-22.5%) of the total global historical production.

3.2 Global consumption

Information on imports, exports, consumption, as well as restrictions on production and imports of PCBs was also compiled for individual countries. These data, along with assumptions on the trade of PCBs (including goods containing PCBs) between countries and regions was utilised to derive an estimate of the global historical consumption pattern for PCBs (Breivik et al. 2002a). As the amounts of PCBs produced in Poland were relatively minor, we assume that all PCBs that were produced in Poland (Table 1) were used within the country.

3.3 Emissions

The first inventory was developed taking advantage of empirical data related to production, consumption and emissions of PCBs alone. Hence, no attempt was made to assess how the predicted emission data would compare with any PCB mass balances derived from environmental observations, e.g. as done by Brzuzy and Hites (1996) for dioxins. Following the publication of the first emission inventory (Breivik et al. 2002a,b), several independent studies have taken advantage of these emission data in the context of environmental fate modelling (Wania and Daly, 2002; Wania and Su, 2004; Macleod et al. 2004; Malanichev et al. 2004) and mass balance studies (Axelman and Gustafsson, 2002; Jonsson et al. 2003; Meijer et al. 2003a; Mandalakis et al. 2005). In addition, there have also been studies using the emission data for interpretation of air monitoring data (Mandalakis and Stephanou, 2002; Meijer et al. 2003b; Hafner and Hites, 2003; Jaward et al. 2004a/2005; Hung et al. 2005). Taken together, these independent studies indicate that the lower emission estimate (Breivik et al. 2002b) is less reasonable in terms of absolute emission values (significantly underestimated). Only the results for the default and higher emission estimates are therefore discussed in the following, even though PCB emission data are made available for all three scenarios for consistency (www.nilu.no/projects/globalpcb).

3.3.1 Temporal trends

In general, it is of considerable interest to evaluate how predicted temporal trends in emissions compare with observed trends in the environment. However, this is a difficult task for compounds like PCBs because (*i*) of significant uncertainties in the emission estimates (Breivik et al. 2002b), and (*ii*) these compounds may also have a significant potential for environmental re-cycling / re-emission from secondary sources (e.g. Wania and Mackay, 1993). Secondary atmospheric re-emissions from environmental surface reservoirs have earlier been implicated as the potential key source of current atmospheric levels (Harrad et al. 1994). However, more recent studies aiming to address the relative importance of primary and secondary emissions have suggested that current atmospheric levels of PCBs, even in remote regions, are mainly driven by primary atmospheric emissions (Jaward et al. 2004b; Hung et al. 2005; Gioia et al. 2006). In fact, model simulations used to interpret North American monitoring data has suggested that the rate of atmospheric decline in PCB concentrations is more or less entirely driven by the rate of decline in PCB emissions (Hung et al. 2005). As the primary emissions of PCBs are declining, the effect of secondary emissions (re-volatilisation) would be expected to increase in relative significance, because the fugacity of PCBs in air may be expected to drop faster in response to emission reductions than fugacities in various surface media. In other words, the rate of decline of primary emissions may be buffered by a relative increase in re-emissions of PCBs from environmental reservoirs. Furthermore, predicted changes in emissions are also likely to be influenced by potential changes and significance of various *de novo* synthesis emission processes, which have not been included in these estimates. For these reasons, it may be beneficial to study temporal changes of PCB emissions in urban regions (Jaward et al. 2004a).

Figure 3A shows the projected temporal trend in global emissions of ΣPCB_{22} from 1930 to 2100, according to the default and higher emission scenarios. For comparison, we have also included the predicted emission trend based on the old emission inventory methodology (Breivik et al. 2002b). As can be seen, the predicted differences in emissions for years prior to ~2000 are relatively minor, comparing the old and new methodologies. In comparison, significant differences in predicted emissions are apparent from year 2000 and onwards. Specifically, the steep reductions in emissions are predicted to occur a few decades later, according to the new methodology. The key reason for emissions persisting at a higher level for a prolonged period (according to the new methodology) is that emissions attributed to PCB usage is allowed to occur for an extended time-period, which again is a result of allowing for temporal variability in failure rates (Fig 1). The differences in these two approaches also illustrate some of the significant difficulties and uncertainties in obtaining accurate emissions of PCBs for the current post production period, as it requires an accurate account of the pools of PCBs remaining in usage, decades after the global production ceased. The results with respect to estimated temporal trends are thus highly sensitive to the predicted amounts of PCBs that are remaining in use, which in turn is subject to uncertainties in the assumed temporal variability in failure rates and the assigned use-life expectancies. Furthermore, we observe that these two predictions tend to converge from ~2050 onwards. At this time, no PCBs are assumed left in use, and the remaining emissions are thus attributed to the decaying emissions from soils and landfills alone (see also Breivik et al. 2002b). In other words, emissions are expected to experience a significant decline when the use of PCB ceases (see also 3.3.2).

Whilst there are significant differences between the two scenarios in the absolute numbers presented in Fig. 3A according to the new methodology, the differences in relative changes in emissions between the two scenarios discussed are much less significant (Fig. 3B,C). Both scenarios would suggest that emissions peaked in 1970, which is the same time as the year of peak production. In Fig 3B, the temporal development in annual emissions of ΣPCB_{22} are therefore plotted, scaled to the peak emissions of year 1970. Under the default emission scenario, the decline occurs somewhat earlier, mainly because the use-life expectancies are shorter than the corresponding higher scenario (Breivik et al. 2002b). However, these differences tend to converge after year 2000. For example, the results for 2005 would suggest that the emissions of ΣPCB_{22} are at ~6% and ~11% of the levels in 1970 for the default and higher scenarios, respectively. Another way to display these results is given in Fig. 3C, for which the annual rate of decline is presented for the two scenarios. As can be seen again for the years around 2040/2050, uncertainties remain over when the transition from a "usage driven" emission pattern would change into a "post usage" (disposal) pattern, and how (and eventually if) this would be manifested in abrupt changes in the temporal trend (Fig. 3C). In other words, the steep reductions in emissions that are predicted in Fig. 3C around year 2040/2050 is explained by the final cessation of PCBs usage from the category that has the longest use-life expectancy (i.e. closed systems).

As previously emphasised, the key uncertainties are manifested in the absolute numbers presented, e.g. the fraction of PCBs historically produced that have been emitted into the atmosphere. According to the default and higher emission scenarios, this number is predicted to be 1.27% and 11.53% of ΣPCB_{22} by the year 2000, respectively. Because of the steep reductions in atmospheric emissions that are envisaged for the future (Fig 3C), the fraction emitted is predicted to end up between 1.32% and 12.37% by the year 2100. We note that there are notable differences in this fraction among individual PCBs, reflecting differences in volatility within the group of PCBs.

As previously noted, it should be mentioned that spatial differences in temporal trends of emissions are expected and predicted on a global scale (Breivik et al. 2002b). To demonstrate this we compare emissions for ΣPCB_{22} for the year for which the emissions peaked (1970), as well as the current time-period (2005) as a function of latitude and longitude in Figures 4A and 4B, respectively. It is evident that current emissions are relatively higher between 40 and 60 degrees latitude and 20 and 60 degrees longitude in comparison to 1970. This is mainly attributed to the late cessation of production and new use of PCBs in countries of the former U.S.S.R. Usage and hence emissions are thus expected to continue for a longer period in countries which either used or imported PCBs from producers that were relatively late to end the production of PCBs (Table 1).

3.3.2 Cumulative emissions and contemporary pools of PCBs

Current control strategies seem targeted towards identifying products and waste containing PCBs, aiming at safe disposal and elimination of existing pools of these harmful chemicals. It is possible to analyse the output of the PCB mass balance model with respect to contemporary pools of PCBs and the relative importance of various emission and other fate pathways. In Figure 5, we show the relative significance of various cumulative fluxes of PCBs (including emission fluxes) from the year 1930 until 2005 on a global scale for the default and higher emission scenarios, respectively. The data are presented as percentage of the cumulative production (or consumption) of ΣPCB_{22}, according to the default and higher production scenarios, respectively (see Figure 2). In the following discussion, the results from the higher scenario are included in parentheses to illustrate the variability in outputs.

Overall, 1.3% (11.8%) of the amounts of PCBs historically produced is projected to have been emitted into the atmosphere by the end of 2005. Both scenarios furthermore suggest that atmospheric emissions of PCBs associated with open usage have been the most significant source. However, the results also suggest that circumstances that lead to PCBs being exposed to strong heat (open burning or accidental fires) could have resulted in significant atmospheric emissions. This compares to 80.9% (63.0%) projected to have been subject to disposal, for which 57.2% (51.9%) are projected to have reached landfills. Of the amounts disposed so far, 76.3% (47.2%) is already projected to have been permanently lost (through degradation / burial in landfills, or destroyed following various combustion processes). Both scenarios suggest that a significant amount or 12.9% (16.5%) may still be in use on a global scale, and that most of it remains in long-lived closed systems (see also 3.3.1). This suggest that further efforts to identify and replace equipment containing PCBs that may still be in use, may have the potential to speed up the reduction in future emissions.

4 Discussion

The overall goal of this study has been to present an update of a dynamic mass balance approach aiming at presenting the “big picture” of the global historical atmospheric emissions of selected PCBs. We note, however, that these estimates are still affected by substantial uncertainties, many of which have previously been detailed by Breivik et al. (2002a,b). In simple terms, the uncertainties in production rates for selected PCBs are less than the uncertainties in consumption patterns, which again are far less than the uncertainties in projected emissions. Thus, any further studies aiming to take advantage of some of these data, should preferably use information on production / consumption, rather than emissions, due to the significant uncertainties introduced in the latter exercise. Secondly, we also note that there are features to these quantitative estimates, which are believed to be more reasonable than others, and which thus may provide more useful information for future environmental fate studies. We have shown that uncertainties in temporal trends are large in terms of absolute values, but more likely to be less uncertain in terms of relative changes (Fig. 3). Likewise, estimated spatial patterns on a global scale seems to be in accordance with surface soil data on a global scale (Meijer et al. 2003a) while the observed distinct urban – rural gradients (e.g. Jaward et al. 2004a) seem to justify the use of population density as a surrogate to distribute use and emissions of this industrial chemical within individual countries. Finally, it is encouraging to note that model predictions of congener patterns in remote areas, such as the Arctic, seems to mirror observations (Wania and Su, 2004; Hung et al. 2005), indicating the actual emission fingerprint of key PCB congeners are captured in these estimates. Further environmental fate studies taking advantage of the data presented herein are likely to provide indications on the strengths and limitations of our estimates.

Additional information

Data from this study are available at www.nilu.no/projects/globalpcb/

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Table 1. Total PCB production as reported in the literature (in tonnes).

Producer	Country	Start	Stop	Amount	%	Reference
Monsanto	USA	1930	1977	641,246	48.4	de Voogt and Brinkman (1989)
Bayer AG	West Germany	1930	1983	159,062	12.0	de Voogt and Brinkman (1989)
Orgsteklo	U.S.S.R. (Russia)	1939	1990	141,800	10.7	AMAP (2000)
Prodelec	France	1930	1984	134,654	10.2	de Voogt and Brinkman (1989)
Monsanto	U.K.	1954	1977	66,542	5.0	de Voogt and Brinkman (1989)
Kanegafuchi	Japan	1954	1972	56,326	4.2	Tatsukawa (1976)
Orgsintez	U.S.S.R. (Russia)	1972	1993	32,000	2.4	AMAP (2000)
Caffaro	Italy	1958	1983	31,092	2.3	de Voogt and Brinkman (1989)
S.A. Cros	Spain	1955	1984	29,012	2.2	de Voogt and Brinkman (1989)
Chemko	Czechoslovakia	1959	1984	21,482	1.6	Schlosserová (1994)
Xi’an	China	1960	1979	8,000	0.6	Jiang et al. (1997)
Mitsubishi	Japan	1969	1972	2,461	0.2	Tatsukawa (1976)
Electrochemical Company	Poland	1966	1970	1,000	<0.1	Sułkowski et al. (2003)
Zaklady Azotowe	Poland	1974	1977	679	<0.1	Falandysz (2000)
Geneva Industries	USA	1971	1973	454	<0.1	de Voogt and Brinkman (1989)
Total	**Global**	**1930**	**1993**	**1,325,810**	**100**	

Figure 1. A) Total failure rate of products containing PCBs, predicted as the sum of random failure, infant mortality failure and wear-out failure. B) Illustrative output of the temporal trend in usage, disposed amounts and emissions (in % of the amount introduced for a particular usage in year 1).

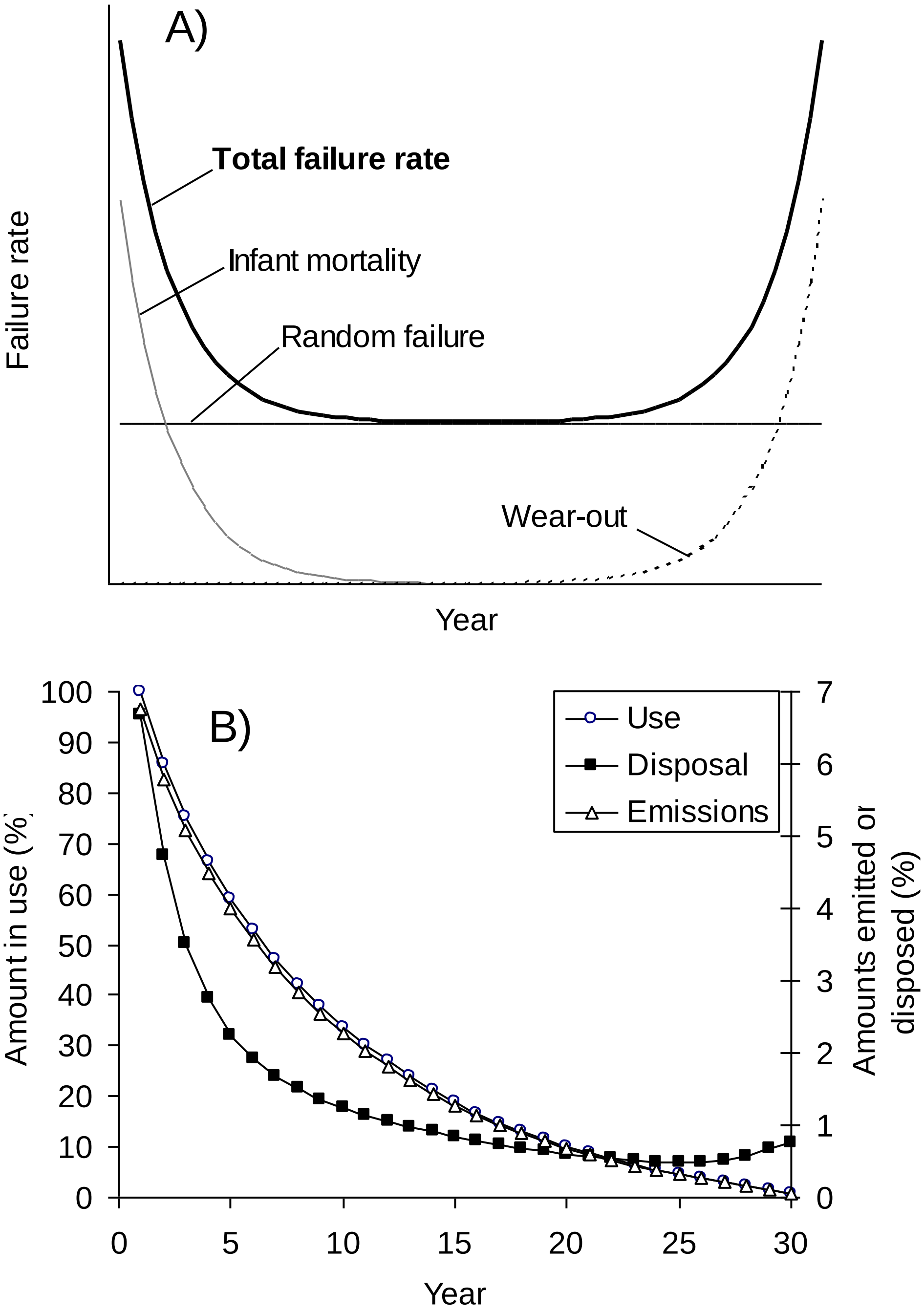


Figure 2. Estimated global historical production of individual PCB homologues (A) and congeners in thousand tonnes.

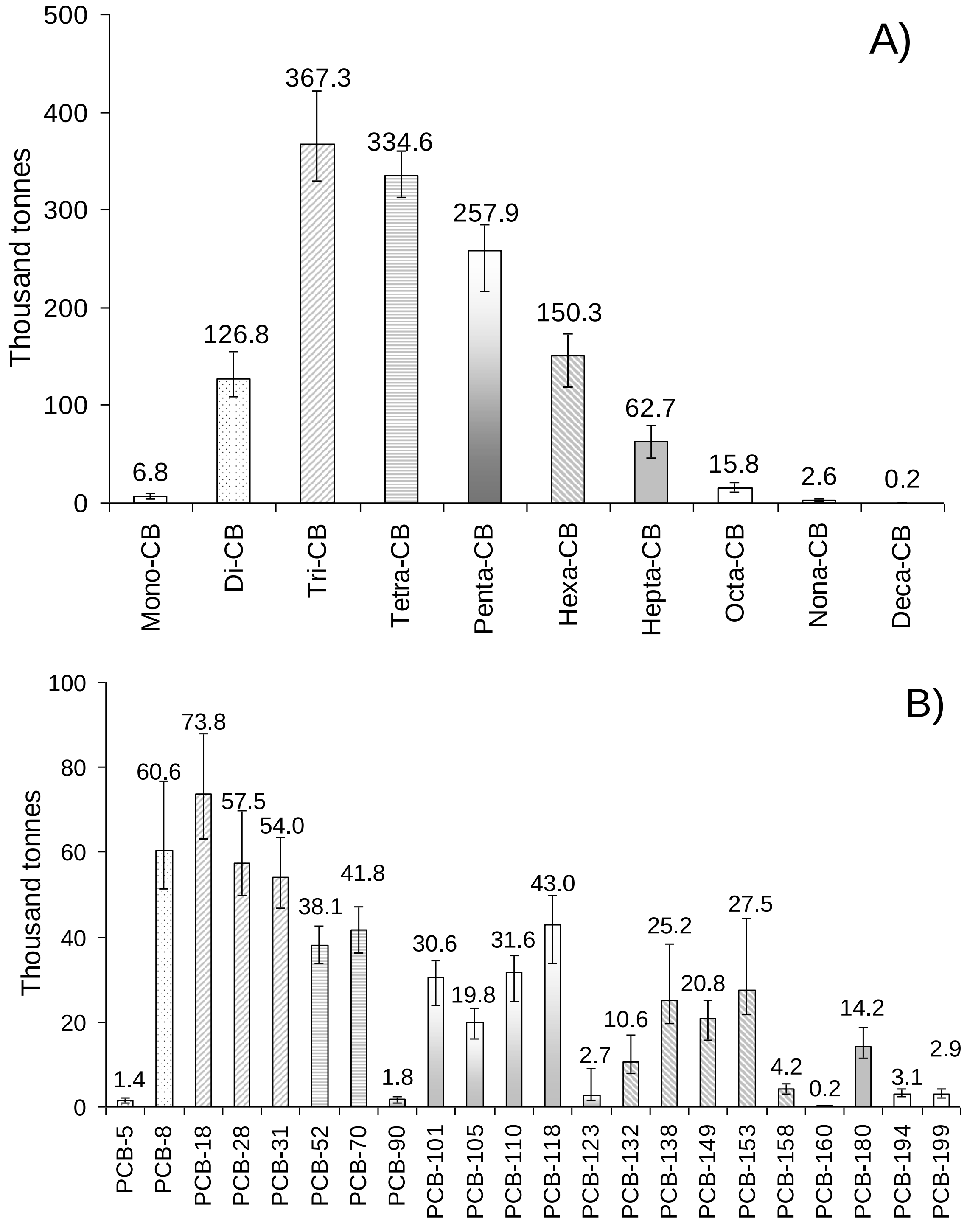


Figure 3. Temporal development of global ΣPCB_{22} emissions according to default and higher emission scenarios, A) illustrating differences in emission inventory methodologies (see text), B) relative to emission levels in 1970 (100%), and C) expressed as annual rate of decline since 1970 (in %).

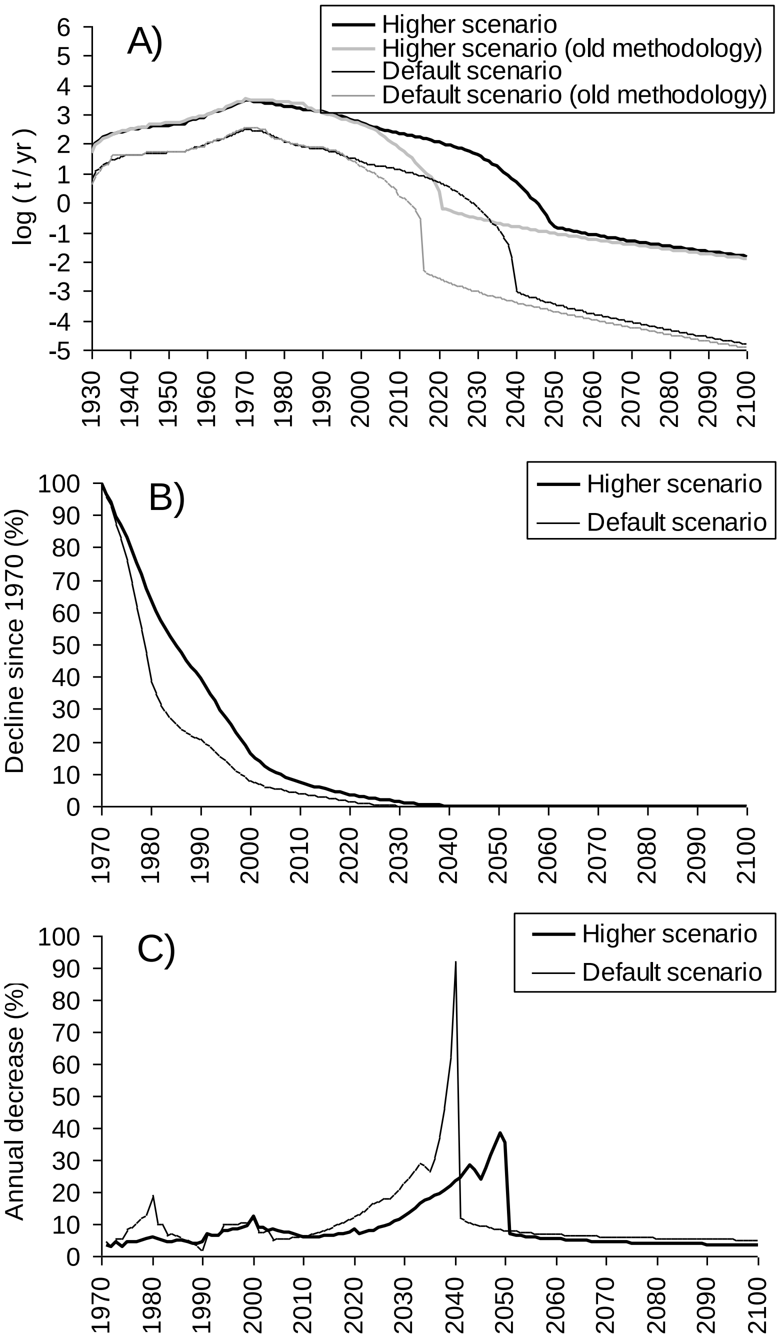


Figure 4. Spatial differences in global emissions of ΣPCB_{22} in 1970 and 2005; A) By latitude, and B) by longitude.

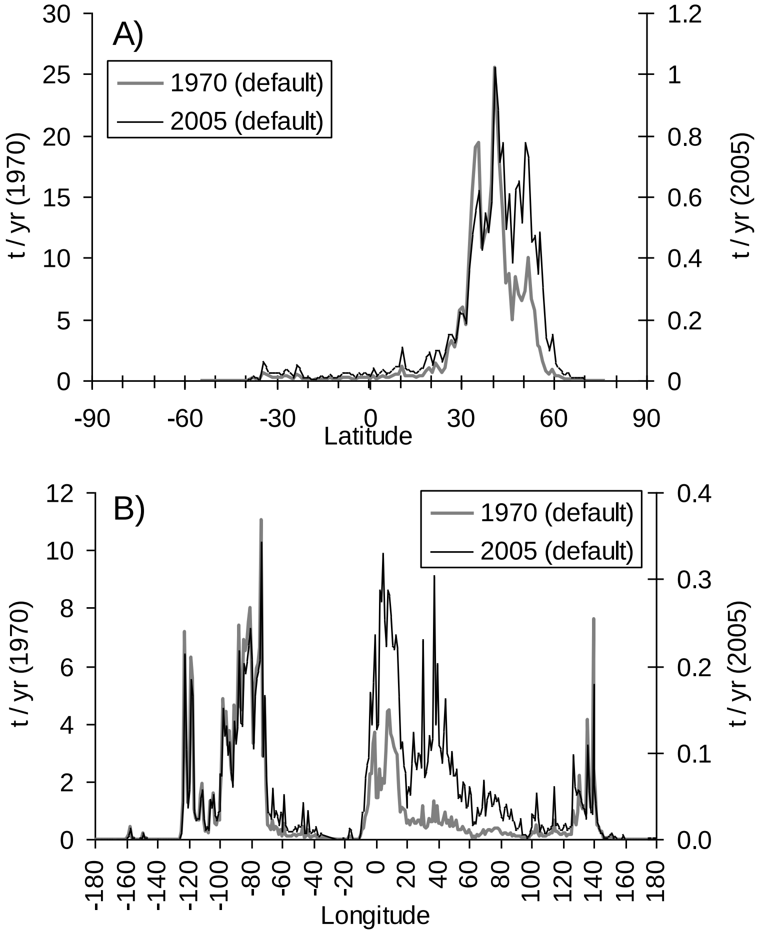
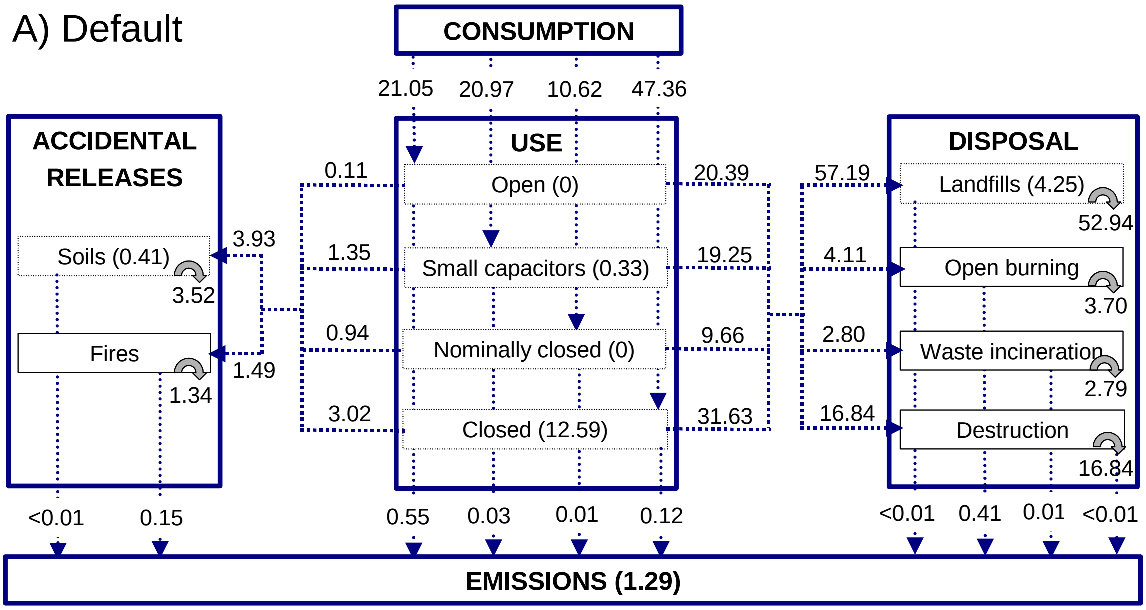


Figure 5. Cumulative emissions of ΣPCB$_{22}$ from 1930 to the year 2005 on a global scale, according to the default (A) and higher (B) emission scenarios. Also given are the predicted pools of various continuous sources (soils, usage categories and landfills) as of 2005. Data are expressed as percentage of the cumulative production of ΣPCB$_{22}$, reflecting the default and higher production scenarios, respectively.

A) Default



B) High