A fugacity model for source determination of the Lake Baikal region pollution with Polychlorinated Biphenyls

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Introduction: PCBs in the Lake Baikal Region

Lake Baikal, located in east-central Asia, is the deepest (1,637 m) and the oldest (25 million years) lake in the world. Almost 20% (or 23,000 km^3) of the earth's non-frozen surface freshwater is contained in its basin. Lake Baikal is a unique ecosystem; 70 % of the species found there are endemic, and it has been designated a UNESCO World Heritage Site.

A group of polychlorinated biphenyls (PCBs) consists of 209 different congeners, many of which are highly persistent in the environment and have been shown to be toxic to wildlife and humans [1]. They were widely used in the 1960's and 1970's, particularly as insulating fluids in electrical equipment, until bans in most industrial countries in the 1980's.

PCBs were discovered in the Lake Baikal ecosystem by Malakhov *et al.* [2] and Bobovnikova *et al.* [3]. A follow up to the initial study showed no decrease over 1981-1989 [4], in contrast to what has been observed in other water bodies in the industrialised world. Further studies also showed the contamination in pinnipeds to be among the highest measured anywhere [5 6 7].

Above studies and other data suggested a presence of a strong local PCB source (or several ones), which has had a widespread adverse effect for the whole region.

To locate the source, Mamontov *et al.* [8 9] collected samples from 34 sites over the region, the analysis of which showed a gradient of a factor of 1000, with the lowest concentrations at the north-east of Lake Baikal and the highest

concentrations close to the city of Usolye Sibirskoye, a centre of the chemical industry in the Angara River valley (Figure 1). A continuous decrease in the soil contamination was observed along the path from Usolye Sibirskoye up the Angara River valley to Lake Baikal and from there north-eastward along the lake. These results indicate that there was (and perhaps still is) a major source of PCBs in the Usolye area, from where the PCBs are dispersed over the region.

However, various obstacles prevent direct observations of potential sources. Therefore, a mathematical modelling approach was adopted in a currently on-going INTAS project aiming to shed some more light on this problem. The model principles, setup and the results of the first experiments are presented in the current paper.

Materials and methods: fugacity model for the lake Baikal region

The key challenge of describing the environmental behaviour of PCBs is the need to consider transport and transformation processes occurring in both the atmosphere and surface media over very long time scales. Because of the long persistence of PCBs in surface media and the reversibility of their atmosphere-surface exchange, accidental releases can influence concentration levels in the regional atmosphere, vegetation, soil and water bodies decades after the release. A fairly simple way to describe these processes is to use a multimedia fate and transport model [10], which consists of well-mixed boxes describing a variety of environmental compartments and links between them representing the migration paths of pollutants between the media.

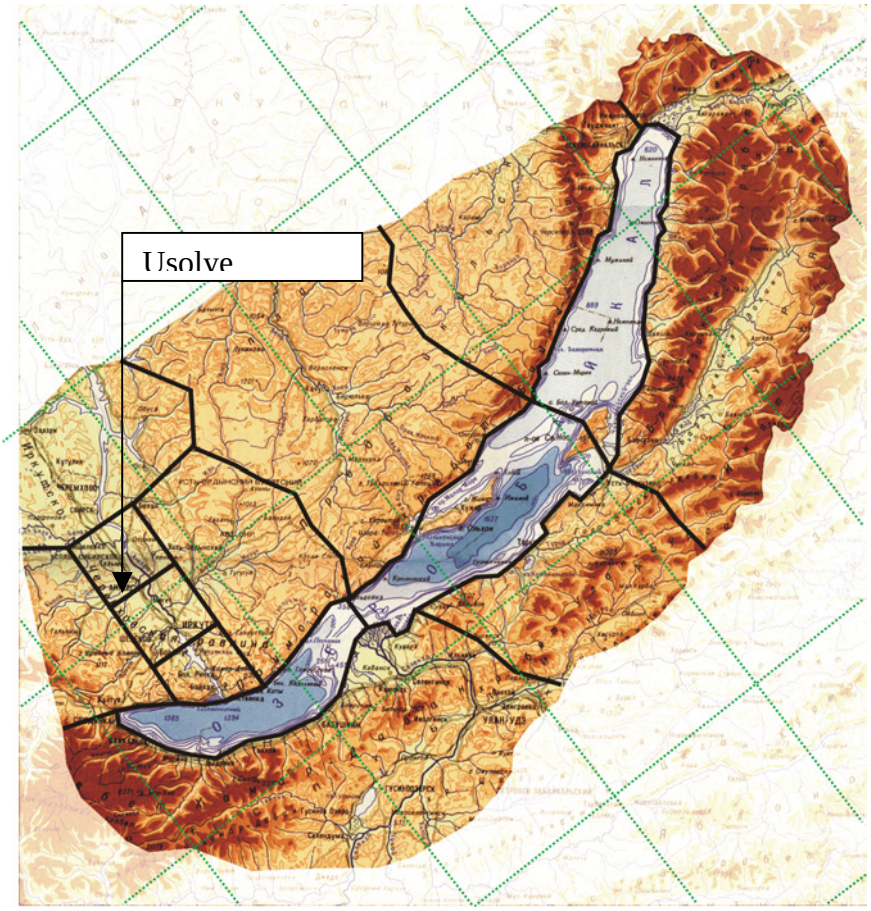

Figure 1. Map of the calculation domain with segmentation into sub-regions.

The fugacity model for the Lake Baikal region is built on the basis of the existing POPYCLICNG-Baltic model of Wania et al. [11]. Similar to POPYCLICNG, it includes atmospheric, aquatic, and terrestrial sub-systems (Figure 2), which are split into several sub-regions (Figure 1). Vertical motion in air is not considered due to the comparatively small size of the region, high uncertainty in the emission source specification, and low resolution of available meteorological data. The atmospheric compartment therefore consists of just one well-mixed atmospheric layer of 1 km height. The description of atmospheric transport is based on

climatological coefficients computed by the dispersion model DMAT [12]. A non-uniformity of the pollution dispersion in the region, as revealed by DMAT computations, justifies the asymmetric split of the domain highlighting the prevailing transport direction (Figure 1).

The aquatic sub-systems describing both Lake Baikal and the Angara River each consist of a stacked column of the bottom sediments and the overlying well-mixed water column. PCB exchange between water and sediment occurs due to diffusion of the dissolved fraction and sedimentation / re-suspension of particulate organic carbon contaminated with PCBs. During winter time the lake is covered with ice, which prevents all water-air exchange from occurring.

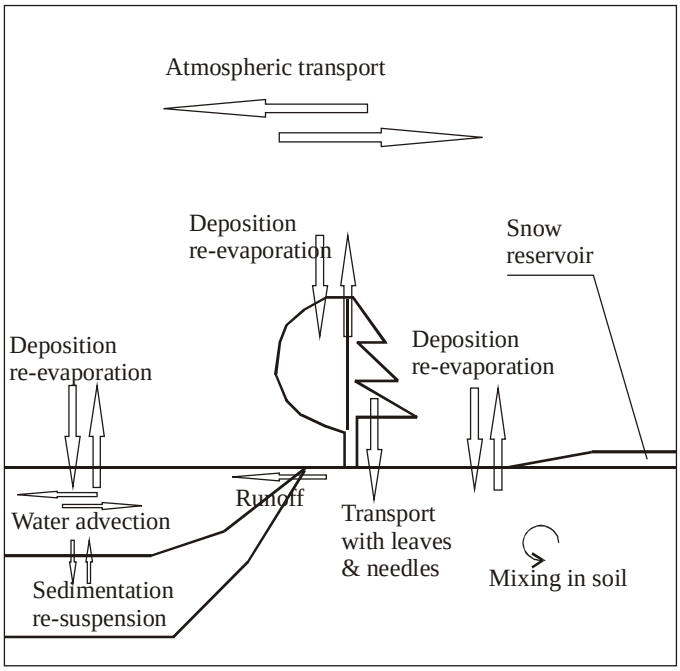

Figure 2. The main model compartments and the chemical exchange fluxes between them.

Terrestrial sub-systems include compartments representing deciduous and coniferous forest, different types of soil and, during wintertime, snow. The water budget within the terrestrial sub-systems and the exchange with the aquatic and atmospheric sub-systems are derived based on literature data on river discharge, precipitation rates (rain and snow) and evaporation. As the next step after the

POPCYCLING-Baltic model [11], the Baikal model explicitly distinguishes between deciduous and coniferous forest and incorporates a dynamical water budget for the region, including the impact of snow and ice on water and contaminant exchange between the surface, water and atmospheric compartments and sub-regions.

The new model is programmed in a manner that provides a high flexibility to the user, allowing changes of virtually all model parameters and modifications of the domain split to sub-regions. This overcomes the corresponding limitations of POPCYCLING, and makes the new model easily adaptable to describing the fate of organic pollutants in other regions.

Results and discussion

A list of possible source types to be evaluated includes the following:

1. Accidental release of a large amount of PCBs into the atmosphere due to an explosion in the past.
2. Permanent atmospheric source, such as a stack of a factory
3. Accidental explosion-type release with mixed atmosphere – soil – water emission
4. Permanent emission into soil, such as contaminated wastes from a factory

Accidental options were included as follow-ups of reports of a major disaster of still unknown character that happened in the beginning of the 80-s reportedly in the vicinity of Usolye. Permanent sources imply currently existing industrial installation(s) possibly using some PCB-based technology. Each of the above source types allows a large variety of characteristics, which are to be identified via model-measurement comparison.

An initial study of the problem was made by means of the DMAT atmospheric transport model without any multi-compartment PCB exchange. The results presented in [13] showed a qualitatively similar pollution pattern to what has been reported by measurements. That study was mainly used for justification of the vertical and horizontal split of the region for the needs of the fugacity model, as well as for compilation of climatological atmospheric transport coefficients.

The easiest to check option in the above list is the first one. For that scenario, the fugacity model showed that for virtually any amount of PCB emitted into the

atmosphere the lasting pollution level is practically insignificant: the total mass of PCB in the region drops below 1% of the emitted mass within a few days, with a nearly complete disappearance by the end of month. Qualitatively, the situation is simple: the size of the region is comparably small, so that the pollution cloud does not stay there longer than a couple of days, which is not enough to generate considerable deposition into soil (the only reservoir capable of long-term storage of the contaminants).

That conclusion, however, can be made only under the assumption that the concentration of PCB in the emitted cloud was well below the saturation level. Otherwise, there may be a “PCB rain” (similar to the well known phenomena of “acid rain”) producing a large amount of PCB deposition in the vicinity of the source. Such an effect is not described by the model and is nearly impossible to parameterize for past events. Instead we included it in option 3 (remains to be explored), which approximates such a release as simultaneous emissions to air, soil, and water. Based on the results above, the mixed-type accidental release can be considered as soil emission only: PCB vapor in the atmosphere will be quickly transported outside the region, while the Angara river flow is opposite to the observed direction of the contamination dispersion (apart from this, PCB species have low solubility in water).

The second set of experiments was made with a permanent atmospheric source located in the Usolye sub-region (Figure 1). An example of the run with constant emission strength is shown in Figure 3. As seen from the figure, the observed nearly-constant amount of PCBs in the region seems to be not exactly met: there is a slow accumulation process, mainly connected with the gradual enrichment of the soil reservoirs with the contaminants. However, after 20 years, the trend is well inside the measurement uncertainty. Indeed, detailed measurements in the region cover the time period of some 10 years, with accuracy of the values within a factor of 1.5 - 2 as the best (apart from the analytical uncertainties due to quite low concentrations, there is also a representativeness error caused by a limited number of sample points). For the same time period (10 years), the model suggests a soil enrichment of 10-20% (as seem from Figure 3), which thus can be easily missed by the observations. Another important parameter, the gradient of the concentrations from Usolye towards Lake Baikal, also seems to be all but missed – the difference between the sub-regions is calculated to be within a factor of 2.5 only (instead of 2-3 orders of magnitude, as recorded by measurements). According to the results, the atmospheric transport in the small region is strong

enough to ensure regional transport well in excess of the observations. Therefore, with a reasonable level of certainty one can conclude that permanent atmospheric source is also not very probable. That conclusion, however, has to be further checked when the refined model version with all important interactions becomes available.

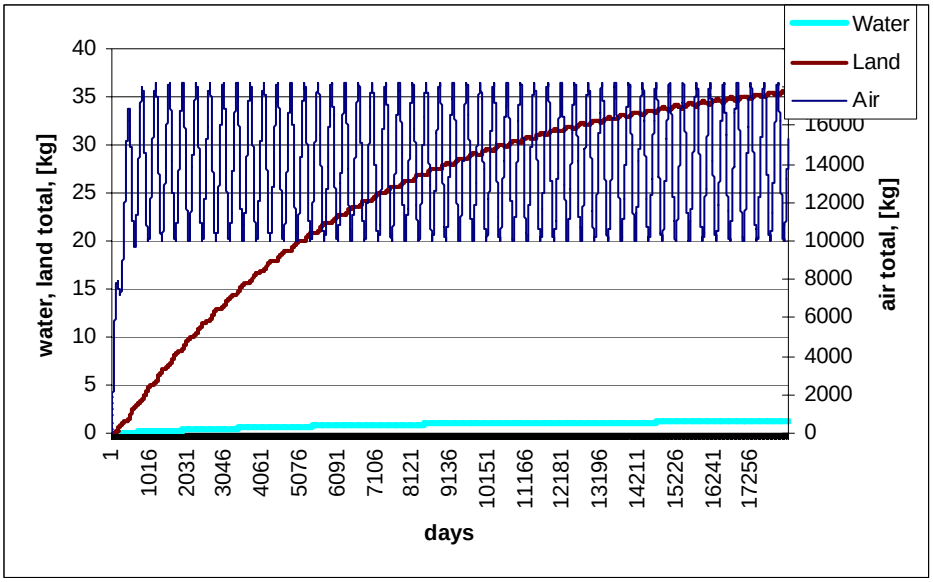

Figure 3. Total mass of PCB-101 in the modeling domain for a 50-year period with a constant emission into air of 10 mole hr^{-1}.

Evaluation of soil-type emission is still to be performed. We will assume that the pollutant was (or still is) emitted directly to soil, with the following gradual evaporation and dispersion around the region. The source may instant or continuous (option 3 or 4) but it is expected that the sharp gradient in soil concentrations will be much better captured by this evaporation-transport-deposition cycle than by a straightforward atmospheric sources assumed in the previous experiments.

If an overall pattern is matched – i.e. the model will report a nearly constant level of pollution in time and a strong gradient of concentrations inside the region – there will be a more tiny criteria: a split of the PCB species along the distance from Usolye. Namely, observations show that the ratios of concentrations of light and heavy PCBs in the vicinity of Usolye and at remote sampling points are

different, with more volatile species prevailing in remote areas. This also indirectly points to a soil reservoir and evaporation process as important parts of the region pollution developments. If some emission scenario will result in similar split between the PCB congeners, it would be a strong reason in favor of the specific type of the source and, consequently, in favor of corresponding scenario of the toxic pollution of the Baikal region.

Acknowledgements

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