Integration of Solid Matter Coupled Contaminant Transport into the 3D Reactive Transport Boxmodel by the Example of PCB in German Hard Coal Mining

Christoph Klinger[1], Michael Eckart[1], Joachim Löchte[2]

[1]DMT GmbH & Co. KG, Geo Engineering & Exploration, Exploration & Hydrogeology, Am Technologiepark 1, 45307 Essen, Germany, Christoph.Klinger@dmt-group.com
[2]RAG Aktiengesellschaft, Health, Safety, Environment, Shamrockring 1, 44623 Herne, Joachim.Loechte@rag.de

Abstract So far, mainly inorganic compounds have been relevant for the evaluation and prognosis of mine water pumped and discharged. In the course of the current closedown of the German hard coal mines, however, substances hazardous to waters must also be taken into account when withdrawing. It was therefore also necessary to consider components from operating leaking fluids in the context of flood predictions. These mostly organic compounds have mobilisation and transport properties completely different from salts. High sorption coefficients lead to high proportions of particle-bound transport. This required a corresponding adjustment of the Boxmodel used in the German coal mining.

Key words Reactive Mass Transport, Modelling, PCB, Mine Flooding, Particle Transport

Introduction

In connection with the withdrawal from still open mine voids and the subsequent flooding, it must be considered that during the mining operation some substances hazardous to waters were used underground. This implies a potential risk within the scope of the flooding, when such substances have leaked and are still present in the mine building. By common classification, the underground generally handled diesel fuel and the used oil are considered to be hazardous to water. This material stock has to be expanded by special additives and various ingredients such as glue, solvents, etc. Substances which can be mobilised therefrom are predominantly mineral oil hydrocarbons.

During active mining but also during and after flooding, such anthropogenic substances can be discharged by means of dissolving and transporting processes with the rising mine water, thus released into the environment. It is important to know the respective chemical properties and relevant mobilisation processes in order to estimate, evaluate, forecast and, if necessary, reduce the discharge of these substances. In the case of particulate bound substances, these properties are completely different from water-soluble compounds. Due to the potential environmental impact of this substance group, the Boxmodel, which is used to describe and forecast mine water rise and water quality (Eckart et al. 2010), has been accordingly enhanced.

Substance relevance and mobility

Mineral oil products which may have leaked into the mining gallery ground are, to a large extent, complex mixtures of mineral oil hydrocarbons with different properties. In particular, diesel oils have relevant water-soluble fractions. Water solubility of these mineral hydrocarbons decreases with increasing molecule length. However, mine water in the German coal mines show only low contents of water-endangering organic substances. This can be seen, for example, in the low concentrations (almost always <0.1 mg/L) of the widespread and comparatively well water soluble mineral oil hydrocarbons in mine waters from already flooded mineworks, in regular monitoring. This value corresponds with environmental regulations. Such low substance contents can be attributed to the fact that also the mineral oil hydrocarbons which predominantly build up the lubricants are well bound to the fine-grained and organic rich substances contained in the gallery ground and are thus only available to a limited extent for a dissolution processes.

The situation is somewhat different for toxic substances whose detection and environmental limits are significantly lower. In German hard coal mining, fire-retardant PCB/PCDM-containing hydraulic fluids were used at Ruhr, Ibbenbüren and Saar from 1964 until 1989. Leaks, defects, etc., led to loss of liquid, so it can be assumed that also some of the PCB-containing hydraulic fluids remained underground. PCBs are toxic and very persistent. On the other hand, they have the high tendency to adsorption especially on organogenically rich solids (LANUV 2015). This leads to low concentrations dissolved in water Measurements at various locations show that PCBs are still present in the mine water (LUA 2015). However, the amounts have now declined so far that identification mostly is conducted via separation of the solid particles contained in the mine water. The PCB content of the solid particles is then determined. Normal water analysis cannot detect these low concentrations. Research is currently under way to determine the amount of PCB truly dissolved in such mine water. However, it is apparent that the larger proportion of the PCB discharge is in particulate form.

Due to this strong tendency of PCBs to bind to particle surfaces, mobilisation and transport of this fraction are fundamentally different from real solutes. Classical transport approaches based on solution and precipitation, such as those known e.g. for salts, cannot be applied here. Not the solubility properties of the organics themselves control the transport process, but rather those of the carrier particles as well as various sorption-desorption equilibria.

It is a prerequisite for the mobilisation of such substances that particles containing PCBs enter the mine water. In contrast to soluble substances, the solids are eroded in turbulent water flow and sedimented again at low flow rates. The processes concerning fine particle transport in a mine are complex and strongly dominated by local and variable processes (mining activity, type of lithology, water level, gallery dip, etc.). Erosion processes (turbulence) are a function of the flow velocity and thus of the local site conditions. Particle coupled PCB release can then only take place in not flooded old (see period of PCB use) galleries in which turbulent flow or mining activity takes place (such erosion channels can be seen in the mines at various points after water entry into inclined sections). Once a gallery is flooded, turbulent flow and mining activities are missing. Flow velocities in such sections are in the range of a few meters per minute, so that a sedimentation of suspended matter is much more probable than re-suspension. This means that water level rise / flooding does not lead to a corresponding deterioration in the quality of the mine water. The operating state is rather the most unfavourable boundary condition for the discharge of such substances.

Model-relevant processes

Water-soluble organic pollutants from operating fluids will behave similarly to geogene substances present in the mineworks. These include easily soluble salts and substances present in pore water. Above all, products of pyrite oxidation such as sulphate and iron are mobilised in solute form. Their mobilisation and flushing behaviour is known and is taken into account by the usual prognosis models. Correspondingly, the development of dissolved organic compounds can be modelled. However, sources are significantly smaller compared to geogene substances.

For an understanding of the transport processes of solid particles with organic substances fixed or sorbed to them and their representation in a model, new parameters must be taken into account. The basic approach is not reversible binding to the solid particles. It is then sufficient to describe the transport of these particles. However, it is also possible in principle to take into account sorption-desorption processes for these mobile particles.

This means that flow velocity and grain sizes must be considered for modelling. There is hardly any information on the grain size distribution of particles contained in the mine water. However, it is obvious that in case of abandoned mines only very small particles can remain mobile after the flow from a distant source to the water discharge due to the low flow velocities in a water-filled gallery. The model concept therefore takes into account three particle fractions. These represent fractions of different properties without specific particle size assignments and can contain a differentiated PCB spectrum. Nearly no sedimentation is assigned to a mobile fraction according to colloidal finest particles.

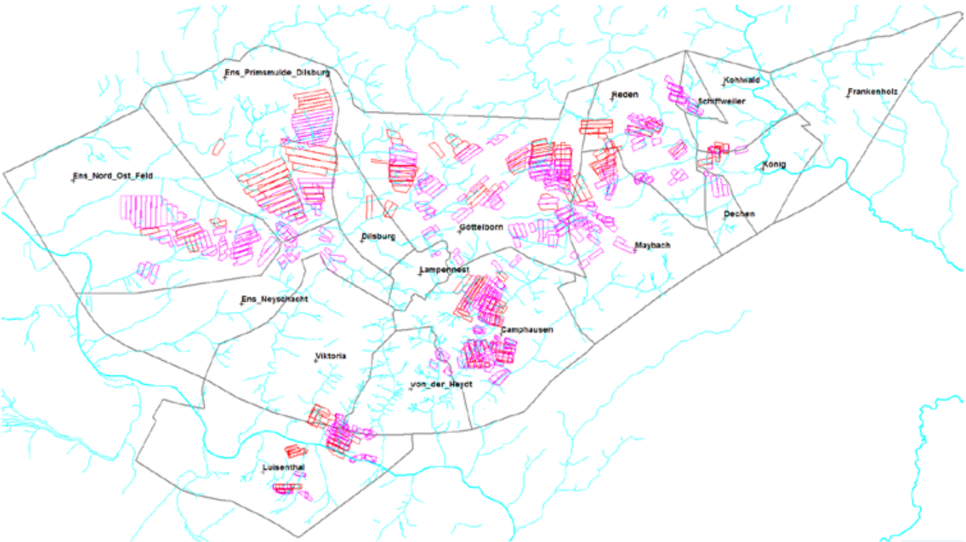

***Figure 1** Large-scale distribution of longwall mining sites with PCB- and PCDM-use at the example of the minefields at the Saar/Germany.*

The model approach considers, according to the data availability, no concrete sites for the spatial allocation and distribution of the PCB sources. A generalised approach is required, which follows the principle of proportionality: where more has been mined with such operating fluids, the probability is higher that PCBs have been emitted and are available as source. Figure 1 shows this geographical distribution of mining sites in the PCB/PCDM time for the site example Saar Area. Using this method, the potential source of the substance for the individual model boxes (slices) can be described in a level differentiated manner (fig. 2). The ratio of PCB-containing and PCB-free particles can be derived from the respective volume ratio in the respective model slice. This value then represents an average value of the very heterogeneous substance distribution and mobilisation potential in reality. In addition, the processes of particle mobilisation and the spatial conditions of a coal mine have to be considered as a function of water level development. This complex system has been described in its components and interactions and transferred to the Boxmodel.

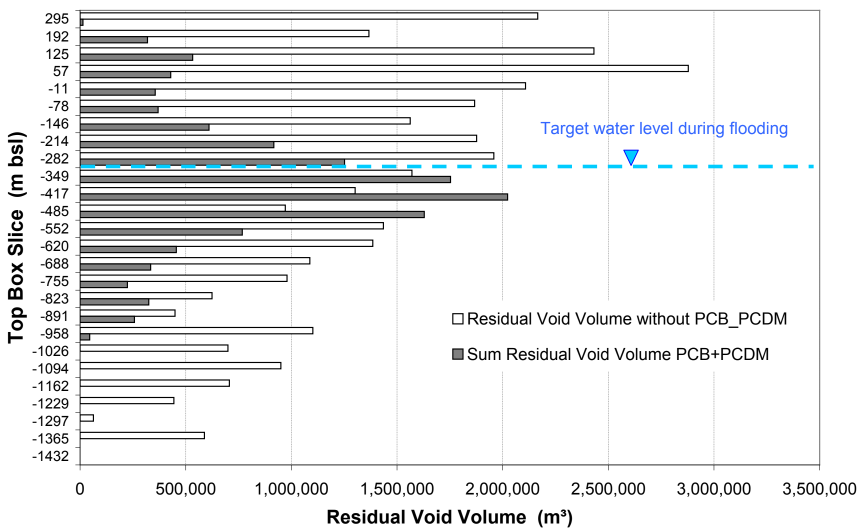

__Figure 2__ Depth distribution of the residual void volume from mining operations within and outside the period of use of PCB/PCDM-containing operating fluids (water province Duhamel / Ensdorf).

Model tool

The box model program BOX3D is used to calculate the non-stationary three-dimensional flow and reactive mass transport (Klinger et al. 2012). It consists of a freely structured model according to the volume balance method, which can take into account defined random geometries (boxes) and a reactive material transport model directly coupled to it. Both models are solved simultaneously. The mass transport model describes the concentration development in the mine water taking into account the release of substances during flooding (e.g., SO_4, Fe, trace metals) and the mixture with geological inflows, which often have high salinity. The mass transport model has reaction terms which can take into account the various sorption and desorption processes as well as chemical reactions between and within phases (dissolution-precipitation reactions). Bacterial processes (e.g., sulphate reduction) can also be calculated as the transport of solid particles, which is quite different from solutes. Based on the calculated flow velocity field, the mass transfer equation (convection equation) is solved in parallel for the liquid phase. Mineral phases were implemented for the solid phase. There may be interactions between the migrants within the liquid, but also between the liquid, gaseous and solid phases.

In the model, the relevant interrelations and substance properties are structured and converted into a calculation concept. This always requires a clear assignment of substance contents to phases, which is not always easy and unambiguous analytically. PCB transport is always particle transport in the current model version due to otherwise missing data and is therefore still considered independent of dissolved substances. A defined PCB content (in µg of congener/kg of suspended matter) is attributed to these particles from the areas which act as the PCB source. The PCB content of this particle is fixed and does not change during transport. When mixing with particle-free mine water, the content of suspended matter (and therefore the PCB concentration in the solid particle phase) is changing but not the transported PCB mass. This PCB load can – by stringent perpetuation of this concept – be reduced only by sedimentation of particles. The sedimentation depends on the type and size of the particles as well as the flow velocity of the mine water on the flow path to the source up to the discharge point. It is assumed that PCBs are predominantly bound to particles which we call “primary” and consist of components (e.g., clay minerals, coal) of the surrounding rock.

The model also takes into account interactions between different particle types. In precipitation reactions, two products are formed: a phase grown on surfaces, which no longer participates in the flow transport process, and fine-grained particulate solids, which are transported with the flowing mine water. PCB-containing solid “primary” particles are subject, in addition to a self-sedimentation, to a co-precipitation with the above-mentioned precipitations (e.g. of $BaSO_4$). This is because it is known that in the case of mineral growth in the solid phase, other components are also incorporated into the mineral matrix. The sedimentation affects the mineral-specific particles originating from precipitation as well as the “primary” particles:

$$R_{Sedimentation} = -k_{Sedimentation} \times c_{Particle} \quad [mg/L/s] \quad \text{(for all particle types)}$$

$$R_{Coprecipitation} = (R_{BaSO4\_directP} + R_{CaCO3\_directP} + R_{FeOH3\_directP}) \times k_{Coprecipitation} \times c_{Particle\_primary}$$

The sedimentation has a clear dependence on the flow velocity. In this respect, empirical correlations to the flow velocity were evaluated and described in terms of the model. In principle, it should be noted that model and measurements have limitations due to the diffuse transitions in the particle sizes. Particles also exist below the pore size of the filters usually used for separating solids. Such colloidal particles can be a few nm in size and thus sediment very slowly. The kinetic approach to the sedimentation calculation in the model takes account of these relationships caused by the grain size distribution and leads to an asymptotic development of the remaining solids contents. This approach is based on the grain size dependencies between sedimentation and transport as depicted in the Hjulstrøm diagram (Hjulstrøm 1935). The result of this dependence of the sedimentation rate on the velocity of the flow is that with increasing water level of the mine an increasing slowdown of the flow conditions begins, the sedimentation effects increase and thus the particle concentrations decreases significantly.

Results

The model was applicated and calibrated for the water extraction from the Saar mines. In addition to usual macrochemical components and trace metals a focus was the solids content and the PCB concentration in the discharged mine water. Here, too, a forecast for the water level rise up to -320 m bsl was derived. Since PCB transport in the mine water takes place via solid particles, these also represent the essential factor for the calibration of the mass transport model. The contents of the filterable substances measured are very low in the discharges of abandoned mines. Figure 3 shows the development for the pumping station Camphausen (Saar). The detection limit is 2 mg/L and most measurements are below this value. However, after an earlier increase in the water level, an initially clearly increased solids content could be observed. This is due to flooding-related changes in the flow regime with the flush of galleries and possibly overflow situations with turbulent flow and erosion. The values then gradually decrease, similar to the flushing curves of sulphate. It can be assumed that the exchange of the particle laden water and sedimentation processes superimpose in the calming water reservoir. Subsequent changes in the measured values due to iron hydroxide precipitation were taken into account.

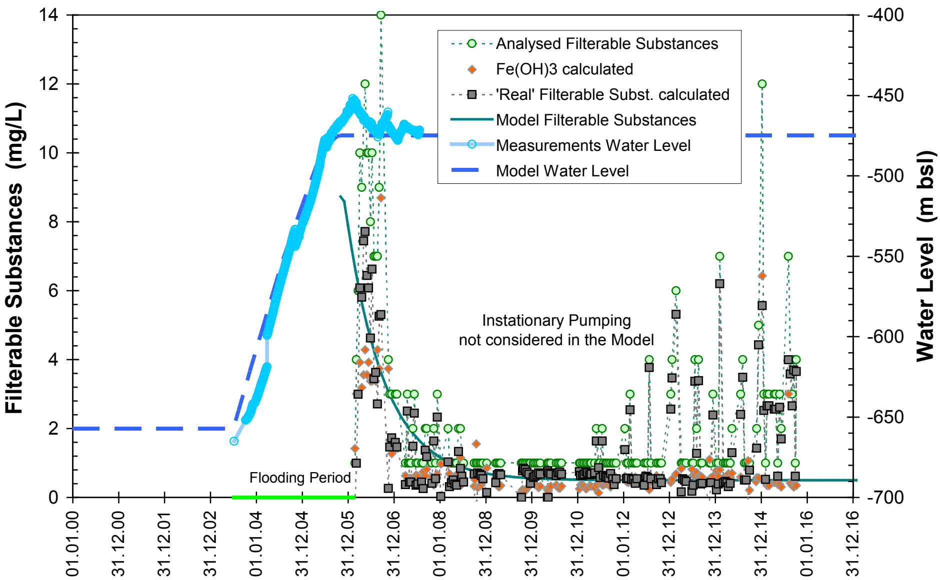

Figure 3 *Measured values for particulate solids in mine water Camphausen with evaluations and calibration of the Boxmodel.*

The level of the PCB content of the particulate solids in the discharges is a result of the proportion of the PCB potential areas (see fig. 1) and is therefore adjusted during calibration. As a result of the PCB examination method (see above) and the low solids contents described, the analysis results vary widely. The analysis data show PCB sum content (6 resp. 7 congeners) between 10 and several 100 µg/kg for the separated solid particles at the pump locations (fig. 4). The available measured values were therefore weighted. The outlier values were ignored, and analyses carried out on larger quantities of material were given some priority for the calibration. The control of the balance of particle concentration (mg/L) and its PCB content (µg/kg) results in the fractions-relevant concentrations (ng/L) calculated therefrom.

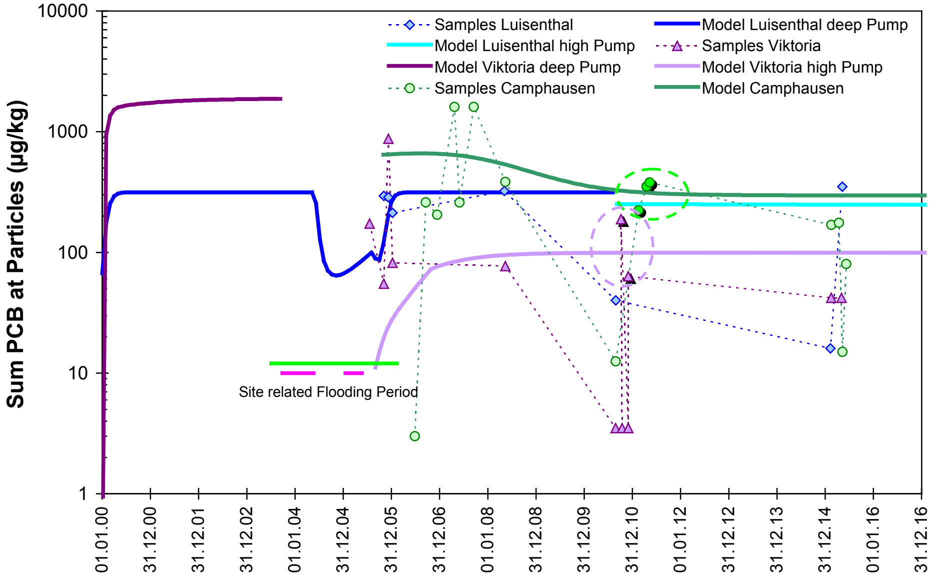

Figure 4 *Measured values for the total PCB content of the particulate solid (= filterable substances) with calibration of the Boxmodel for three Saar pumping stations (Luisenthal, Viktoria, Camphausen).*

The water rise for the investigation area Saar up to the level -320 m bsl will last approx. 3 years. The model results for the PCB discharge (fig. 5) are mainly a result of the behaviour of the solids contents transported in the water. It is expected that the development shown in Figure 3 will be repeated (mobilisation followed by increased sedimentation resp. reduced erosion). The load of the PCBs attached to these solids follows the same processes. Unlike sulphate (and similar salts), the source of the particle bound substance is not below the water level but above it. Water increase thus reduces the potential release. This will lead to a 75% reduction in PCB loads from the study area according to the model projections.

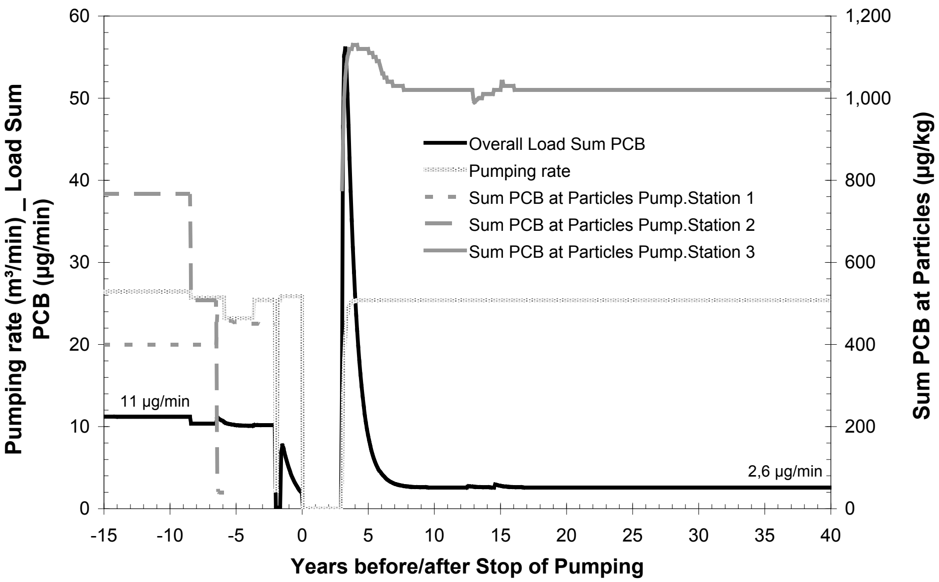

Figure 5 *Model prognosis for the development of the PCB load as well as the determining pumping rates and PCB solids content for the total water extraction in the Saar model area.*

Conclusions

Basis for the modelling of the PCB output is the modelling of mobilisation and sedimentation of particles in the course of water flow in the mines. As a result, it seems plausible that water level rise reduces the mobilisation potential for PCBs. PCBs are obviously mobilised, as long as the relevant mine cavities are not yet flooded. Flooding of a PCB contamination in a gallery ground prevents turbulent flow and thus detachment of particles from the floor. In order to minimise such particle bound pollutants, therefore, keeping the water level down is the wrong strategy. Water rise with the highest possible water levels, on the other hand, neutralises the PCB source and in addition reduces the amount of water and salt water discharged. Results for this particle-bound transport are also applicable to other higher molecular weight organic compounds because they are also as dominantly bound to fine particles as PCBs. The model concept can also take into account the sorption / desorption processes to which such substances are subject.

References

Eckart M, Rüterkamp P, Klinger C, Kories H, Gzyl G (2010): Qualitätsentwicklung der Grubenwässer bei der Flutung von Steinkohlen- und Erzbergwerken. Merkel, B.J. & Schipek, M. (eds.): Grubenwässer – Herausforderungen und Lösungen, 61. Berg- und Hüttenmännischer Tag, 123-131, TU BA Freiberg

Hjulstrøm, F. (1935). Studies of the morphological activity of rivers as illustrated by the River Fyris. Bulletin of the Geological Institute, 25, 221–527. University of Uppsala

Klinger C, Charmoille A, Bueno J, Gzyl G, Garzon Súcar B (2012): Strategies for follow-up care and utilisation of closing and flooding in European hard coal mining areas. International Journal of Coal Geology, 89, Special Issue European Coal Conference 2010, 51 – 61

LANUV (2015): Belastungen von Oberflächengewässern und von aktiven Grubenwassereinleitungen mit bergbaubürtigen PCB (und PCB-Ersatzstoffen) – Ergebnisse des LANUV-Sondermessprogramms 2015. Landesamt für Natur, Umwelt und Verbraucherschutz NRW, 38 pp

LUA (2015): Stand der PCB-Belastungen in Saarländischen Fließgewässern (Schwebstoffe und Biota). Landesamt für Umwelt- und Arbeitsschutz des Saarlandes, Geschäftsbereich 2 Wasser, Fachbereich 2.4 Gewässerökologie, Bericht 2.4 – 2015 – 01, 42 pp