Biological Treatment of Mining Impacted Groundwater and Streams – an Option to Meet European Legal Standards?

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Abstract
This study evaluates the potential for biological treatment methods to achieve a good quality status for water bodies in Saxony (Germany). Generally suitable methods were classified in engineered ecosystems, technical reactors and subsurface in-situ technologies. These utilize either iron oxidation or sulfate reduction as the core microbial process. Broad application to mitigate the long-lasting and widespread mining impact in Saxony seems limited. Some of the delineated obstacles are: economic limitations due to the amount of carbon source necessary to stimulate sulfate reduction at the affected scale; long term instability of sulfides in naturally aerobic systems; low reaction rates in winter.

Keywords: Water Framework Directive, good status, sulfate reduction, iron, metal(iod-)s, Saxony

Introduction
Mining has a century-old tradition in Germany's federal state of Saxony (Kugler 2008). Till today this affects the quality of surface waters and groundwater. Caused by the accompaniment of the mined raw materials with sulfidic minerals, the contamination is typically characterized by acidic conditions, elevated concentrations of sulfate, iron, other metals or arsenic.

With the adoption of the European Water Framework Directive (WFD, European Parliament 2000) the priority of water protection increased for the member states of the European Union. Using a cross-border approach, catchments of groundwater and surface water were divided in so-called water bodies, which must achieve a good chemical and ecological status latest by 2027. By the reference year 2015 this was not met for 59 % of the groundwater bodies (related to the surface area) and 99 % of the streams (related to stream length) in Saxony.

In this study the applicability of biological treatment methods for mining impacted water was assessed on typical Saxon conditions. For this purpose the work was structured in the following tasks: a) delineation of legal standards that relate to mining activity in Saxony, b) characterization of the state of surface and groundwater bodies for these quality components in Saxony, c) review of biological treatment methods for these components, d) review and assessment of already existing biological mine water treatment in Saxony.

Methods
As stated above, the presented work can be divided in four tasks with the following approaches: In order to determine which parameters are affected by mining at one hand and are potentially responsible for the poor status of water bodies in Saxony at the other hand, the relevant legal basis was assessed and brought together with the general geological and geochemical conditions in the region.

In a second step mining affected water bodies were characterized regarding to long-term concentrations of these mining related compounds. Concentrations at 1908 surface water and 3026 groundwater observation points were provided by the Saxon State Office for Environment, Agriculture and Geology (LfULG). First a temporal aggregation was conducted for all observation points by calculating average long-term concentrations (1990-2017 for groundwater, 2000-2017 for surface water). Subsequently a spatial aggregation on these average concentrations over the water bodies was performed by calculating average values and percentiles. As the number of observation points in surface water bodies often does not exceed five, only average values were calculated for them. To characterize hot-spots of contamination, where a treatment would be potentially located, 90 percentiles were used for the groundwater bodies. Maps were created that visualize these concentrations and in which degree they exceed legal standards and later used to group surface and groundwater bodies in so called 'stress groups'.

For Saxony's mining related contaminants derived above, the international literature on biological treatment methods was surveyed. Focus was set on real treatment applications and their economic feasibility. Promising biological treatment methods were described, classified and evaluated with respect to their specific applicability under conditions in Saxony.

In a last step available literature about already existing biological mine water treatment in Saxony was evaluated. Technical and economic key performance parameters were compiled as well as the reasons for eventual termination.

Mining related water contamination spectrum in Saxony

Provisions of the WFD are transposed into federal German legislation by the Groundwater Ordinance (Grundwasserverordnung, GrwV) and the Surface Waters Ordinance (Oberflächengewässerverordnung, OGewV). In these ordinances limiting concentrations for hazardous components are defined. These are to consult to determine the good or bad status of water bodies. In order to select those quality components that are related to mining activities in Saxony the following criteria were applied: Raw materials mined in Saxony comprise lignite (Lusatian and Middle German district), hard coal, and ores of e. g. silver, uranium, zinc (Ore Mountains region). As lignite is accompanied by iron sulfides and as ores are mostly sulfidic minerals, mining caused formation of acid mine drainage (Blowes et al. 2014). Especially in the Ore Mountains region acid mine drainage also contains non-iron metals and metalloids. Figure 1 summarizes quality components in the two ordinances that can be attributed to mining effects in Saxony.

Characterization of surface water and groundwater bodies

By the year 2015, 24 of the 83 Saxon groundwater bodies and 122 of the 746 surface water bodies were in a bad chemical or ecological status due to mining related contamination. Their location correlates to the three main mining regions: Lusatian lignite district, Middle German lignite district and Ore Mountains region. Additionally, surface water transports contamination northward with the main flow direction. Figure 2 and figure 3 show the location of the mining affected water bodies with their mining related contamination spectrum (stress groups). Whereas in the lignite mining areas the legal

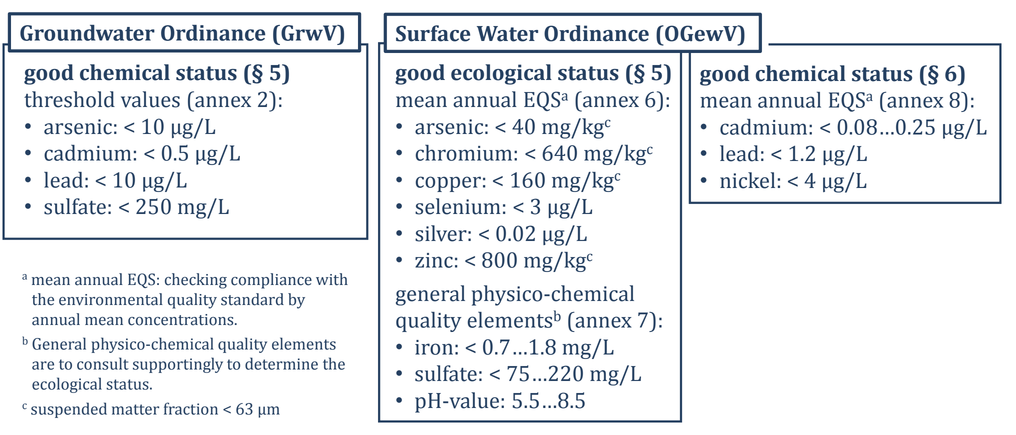

Figure 1 *References for mining related quality standards of surface and groundwater in German legislation.*

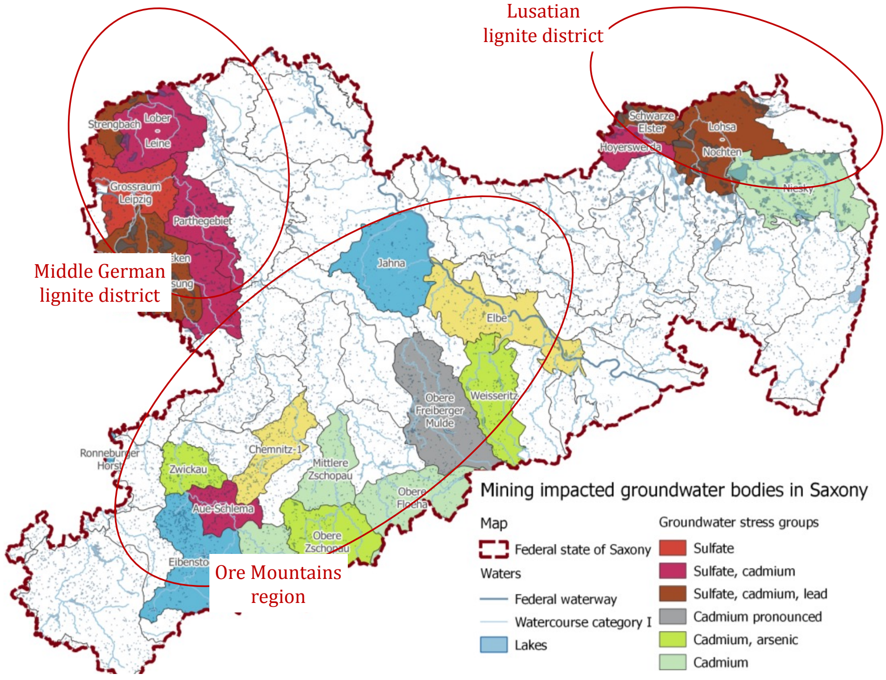

Figure 2 *Groundwater bodies in Saxony grouped by their contamination with mining related compounds. The 90 percentile of long term annual mean concentrations (1990-2017) of all monitoring points in a groundwater body exceeds the threshold value of the GrwV.*

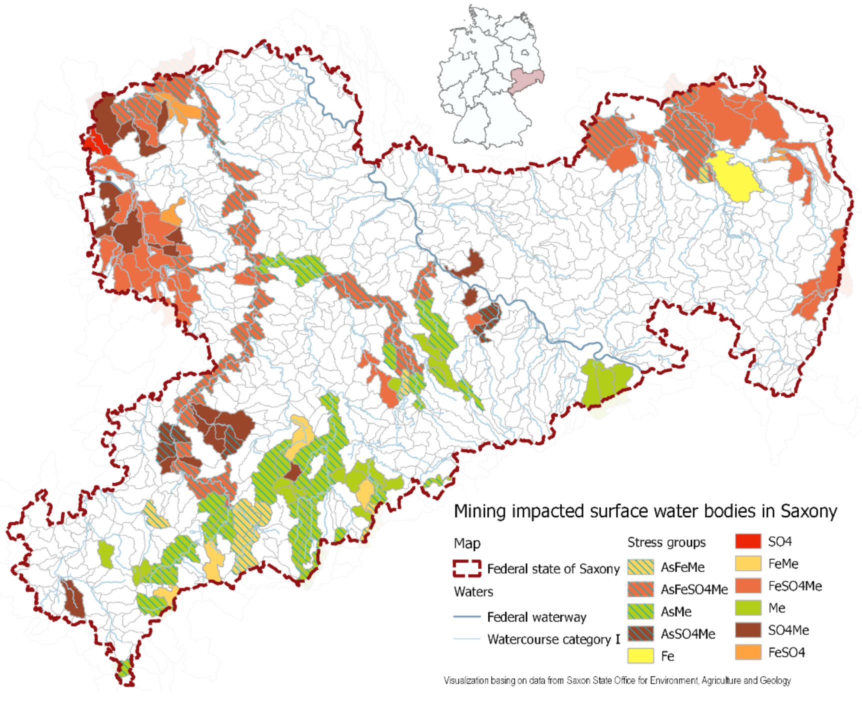

Figure 3 *Surface water bodies in Saxony grouped by their contamination with mining related compounds. Long term average concentrations (2000-2017) of all monitoring points in surface water body exceed threshold values of the OGewV. Me: metals including copper, nickel, lead, cadmium, zinc.*

standards of sulfate and metals are exceeded, water bodies in the Ore Mountains are mainly only contaminated with metal(oid-)s. Arsenic exceeds environmental quality standards in surface water bodies rather evenly.

Review of biological mine water treatment methods

Biological mine water treatment methods were defined to include all methods whose core process rely on the direct utilization of (micro-)biological metabolic processes or, indirectly, their geochemical effect. Above delineated mining related contaminants are all inorganic and thus, with the exemption of sulfate, cannot be degraded, but only be transformed into less mobile forms (immobilization).

With respect to utilizable biological core processes, microbial sulfate reduction (heterotrophic or autotrophic) and microbial iron oxidation are to consider. By stimulating one of these metabolic processes an often complex network of geochemical reactions is induced, including mineral dissolution/precipitation, sorption or further redox reactions. Also purely physical processes support remediation (e.g. filtration). The specific manifestation is strongly dependent on site specific conditions.

For further handling, the assessed mine water treatment methods were grouped by their core technology. Regarding those biological treatment methods that are potentially applicable under Saxony's conditions, these three groups comprise:

a) **Engineered ecosystems** have contact to the atmosphere and are unprotected against climatic influences (constructed aerobic or anaerobic wetlands).
b) **Technical reactors** are constructively closed reaction rooms for a (micro-) biologic community under more controlled conditions (reactors for microbial auto-/heterotrophic sulfate reduction or iron oxidation).
c) **Subsurface reactors** are installations, that supply a reactive medium to the aquifer and use the downstream aquifer as reaction room for the initiated microbial processes (reactive barriers including funnel-and-gate concepts, reactive zone technologies).

No standardized nomenclature for these methods exists. The majority of literature sources published lab scale or bench scale experiments, which were not assessed for this study. Only few publications show performances of existing treatment plants and even less specify figures on (long term) economic feasibility or pitfalls.

Experiences and perspectives for biological mine water treatment in Saxony

Until today seven pilot treatment plants were operated in Saxony that utilize biological treatment methods. At the current state none of them will be further developed to full scale by the remediation agencies. Table 1 summarizes location, treatment target, technology and, as far as known, the reason for termination.

Six of the plants listed in Table 1 are located in the lignite mining districts with the focus on treatment of iron and sulfate. Many of them base on heterotrophic sulfate reduction as core process and therefore depend on the supply of a carbon source. The ratio of carbon to sulfate is determined by reaction stoichiometry and therefore limits economic feasibility at the current price of utilizable and regulatory approvable carbon sources. A further characteristic for treatment attempts in the lignite mining areas is the focus on treatment of groundwater flowing into surface streams or water at discrete lake discharges. This reflects the effort of the responsible remediation agency, LMBV mbH, to lower contaminant fluxes into surface streams. Treatment of mining affected groundwater itself on larger scale is not emphasized, as the area of former groundwater draw down altogether covers about 3000 km².

In the Ore Mountains region, with its stronger metal contamination, only one biological pilot plant was operated (Pöhla). Presently the responsible remediation agency, WISMUT GmbH, operates six chemical treatment plants for mine water (mainly heap leakage and waters from pit flooding). Their economic feasibility and secure process control outcompete biological treatment options so far.

***Table 1** Field and pilot tests of biological mine water treatment in Saxony. [a]: Plant comprised multiple treatment trains; the one including the biological core process is listed. [b]: Schöpke (2011), [c]: FIB (2018), [d]: Bilek & Wagner (2012), [e]: BioPlanta (2012), [f]: GEOS (2017), [g]: Schöpke (2008), [h]: Kießig et al. (2004) hSR: heterotrophic sulfate reduction, aSR: autotrophic sulfate reduction, FeOx: microbial iron oxidation.*

Site Source	Target contaminants	Technology	Status and period of operation	Reason for termination
Skadodamm[b]	Fe, SO_4	funnel-and-gate, in-situ injection of glycerin, hSR	pilot plant 2008-2010	economic feasibility
Ruhlmühle[c]	Fe, SO_4	in-situ injection of glycerin, nutrients, hSR	pilot plant 12/2014-07/2017	economic feasibility
Burghammer[d]	Fe, SO_4	on-site bioreactor for aSR with generation of H2a	on-site test 01/2011-01/2013	realization of pilot test suspended
Hainer Lake[e]	SO_4	on-site fixed-bed reactor with gravel and granular iron, molasses, hSRa	on-site test 06-12/2011	strong T dependence, increased effluent iron concentrations
Tzschelln[f]	Fe	chemolithotrophic schwertmannite precipitation	pilot plant 10/2006-10/2007	utilization of Fe-product not yet competitive
Senftenberger Lake[g]	Fe, SO_4	in-situ injection of methanol, nutrients, hSR	pilot plant 09/2000-12/2003	not known
Pöhla[h]	As, Fe, Mn, U	aerobic constructed wetland, FeOx	pilot plant 2004-2014	failed to meet target concentrations; high maintenance and costs

Generally, most of the biological treatment methods could reduce concentrations of target contaminants. Each of the methods has its specific capabilities and limitations that are further restricted if effluent concentrations are to meet regulatory limits for the good status (Figure 1). To summarize, the following perspectives and limiting conditions were derived from experiences in biological mine water treatment in Saxony:

1. Related to chemical treatment, specific space requirement is increased due to lower **reaction rates**. Further, biological reaction rates show higher temperature dependencies. Especially in the Ore Mountains region, this may bring surface water treatment to cease during winter.
2. Biological mine water treatment methods do not per se have lower **maintenance costs** than chemical treatment methods have.
3. Immobilization of metal(oid-)s creates **sludges**, sediments or geological bodies enriched in these contaminants. Long term possibilities for utilization, disposal or protection against redissolution must be found. This limitation also affects non-biological treatment methods.
4. All treatment methods based on hetrotrophic sulfate reduction need a microbially utilizable and regulatory approved **carbon source**. For flown through solid media these should also be long-term permeable for years. Economically feasible substances, for which durable discharge into water is expected to be regulatory permitted, are not known at the present time. As a rule-of-thumb the costs for carbon source alone account for 0,5…1 € per kg sulfate.
5. Microbial sulfate reduction requires absence (or if not given, removal) of oxygen and nitrate in the water to treat. Surface waters and partly groundwater in Saxony are naturally **aerobic** which implies additional effort to implement sulfate reduction.
6. All in-situ methods utilizing sulfate reduction are perceptible for **redissolution** of sulfidic precipitates as soon as anaerobic conditions cease after treatment (Vandenbohede et al. 2019).
7. Treatment of contaminated rivers or streams offers another constraint: Most of the contaminants considered here (metals, metalloids) are **sorbed at particular matter** of the stream bed. Dynamic equilibrium between dissolved and sorbed metal(oid-)s would obliterate any treatment of water alone.

Potential application of biological treatment for mining impacted water in

Saxony is seen for local hot-spots, as for example heap leachate with constructed wetlands or in-situ methods for highly contaminated groundwater streams. Layout of the treatment technology as well as economic feasibility depend on the specific site conditions at one hand and future development of official regulations and prices at the other hand.

Conclusions

There are numerous examples for successful biological mine water treatment worldwide (e.g. Skousen et al. 2017). However, in summary the following obstacles hinder broad application of biological mine water treatment under conditions in Saxony: a) economic boundary conditions (e.g. price for approvable carbon source), b) often lower process control compared to chemical treatment, and last but not least c) the sheer extend of contaminated water volumes, with often no distinct contamination hot-spot; where the latter point is valid for any treatment technology.

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