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Evaluation of Treatment Techniques for Mercury Contaminated Leachates

Master of Science Thesis in the Master's Programme Environmental Measurements and Assessments

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Cover:
View over the Välen mud deposit site, Göteborg, Sweden, 2011.

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ABSTRACT

Leachate from the Välen mud deposit site is contaminated with mercury and other hazardous metals. The condition of Välen bay does not fulfill a good ecological status why point sources in the vicinity need mitigation measures in order to obtain a better water quality. This thesis investigates potential water treatment techniques with focus on mercury removal at Välen. Various techniques are researched in a literature study and a pilot plant is conducted on site with activated carbon columns. The daily leachate flow is also measured that goes untreated to the bay via a sludge well on site. Treatment techniques studied are: adsorption, precipitation/co precipitation, ion exchange, membrane filtration, phytoremediation, biosorption and bioaccumulation. The site applicability of these techniques at Välen is evaluated and the techniques are compared based on criterion to see which of them that is the most appropriate to be used at Välen in the future.

The average daily inflow that reaches the sludge well was 0.1 m^3/day which constitutes only 0.3 % of the amount leachate formed at the site. Hence the leachate leaves the site at other locations which are unknown. The column test showed that breakthrough for total mercury was not reached within 30 days (150 bed volumes) which was due to the lack of water to the sludge well and too low flow through the columns. The removal efficiency for mercury and other metals was good but seldom enough to have effluent concentrations below the environmental quality standards or guidelines.

The outcome of the comparison of the treatment techniques from the theoretical study showed that adsorption with activated carbon and biosorption were the best. This was based on criterion such as; cost, functionality, efficiency and eco friendliness.

The conclusion is that further studies are needed in testing activated carbon and biosorption materials as peat at laboratory followed by another field pilot test to reach breakthrough and estimate dimensions and costs for a potential full scale facility. A more in depth site investigation is required in order to see improvements to relocate and collect more leachate to the sludge well before installing any treatment technique.

Key words: mercury, leachate, adsorption, chelating resins, biological treatment, removal efficiency, breakthrough.

Utvärdering av reningsmetoder för kvicksilverförorenat lakvatten
Examensarbete inom mastersutbildningen Environmental Measurements and Assessments

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SAMMANFATTNING

Lakvatten från Välen mudderdeponi innehåller kvicksilver och andra farliga metaller. Välenviken uppnår i dagsläget inte en god ekologisk status och åtgärder bör därför vidtas för att reducera utsläppskällor runt om viken för att säkerställa en bättre vattenkvalité. I detta examensarbete genomfördes en studie om olika reningsmetoder för att rena lakvatten från kvicksilver vid Välen mudderdeponi. En litteraturstudie utfördes för att jämföra olika reningsmetoder och en pilotanläggning med kolonner packade med aktivt kol testades på plats med lakvatten från Välen. Det inkommande lakvattenflödet till slambrunnen uppmättes, vilket i dagsläget går orenat ut i viken efter slambrunnen. Reningsmetoderna som studerades var: adsorption, kemisk fällning/koagulering, jonbytare, membranfiltrering, fytoremediering, biosorption och bioackumulering. Tillämpligheten för de olika metoderna på Välen analyserades och jämfördes sedan baserat på några utvalda kriterier för att bedöma vilken metod som är mest lämplig att potentiellt användas på Välen i framtiden.

Det uppmätta lakvattenflödet till slambrunnen var i medel 0.1 m^3/dag vilket utgör endast 0.3 % av den dagliga lakvattenbildningen på platsen. Detta betyder att deponin har ett omfattande diffust läckage av lakvatten. Under kolonnförsökets 30 dagar (150 bäddvolymer) nåddes inte genombrott för totalt kvicksilver, vilket berodde på det låga inflödet till slambrunnen och därmed ett för lågt flöde genom kolonnerna. Kolets reningseffektivitet var hög för metaller inklusive kvicksilver, men var dessvärre sällan tillräckligt för att åstadkomma från kolonnerna utgående koncentrationer under riktlinjevärdena. Från jämförelsen mellan de olika reningsmetoderna visade det sig att adsorption med aktivt kol och biosorption var de bästa metoderna baserat på de olika kriterierna som var: kostnader, användarvänlighet, effektivitet och miljövänlighet.

Mer ingående studier om sorptionfilter med aktivt kol och möjligen biosorptionsmaterial som till exempel torv bör göras inledande i laboratorium och därefter vidare som nytt pilotförsök i fält. Detta för att säkerställa att genombrott nås för att bestämma kostnader och dimensioner för en reningsanläggning i fullskala. Även en mer djupgående studie bör göras på platsen för att söka ta reda på var lakvattnet lämnar deponin och för att se hur mer vatten kan ledas till slambrunnen innan någon teknik installeras på platsen.

Nyckelord: Kvicksilver, lakvatten, reningsteknik, Välen mudderdeponi, adsorption, jonbytare, effektivitet, genombrott

Preface

The Master’s Thesis comprises 30 Hec and has been carried out from February to August 2011. The work load has been equally divided between the authors of this report. Re the Kretsloppskontoret’s request, the thesis was conducted with the supervision of Chalmers University of Technology.

This master’s thesis was accomplished with the sincere and profound supervision of Associate Professor Ann-Margret Strömvall and Assistant Professor Yuliya Kalmykova. We would particularly like to thank research engineer Lars-Ove Sörman for his extraordinary guidance during the pilot plant installation. We genuinely offer our gratitude to Mona Pålsson, for her supervision in lab tasks and Elisabeth Porse from Kretsloppskontoret for her thoughtful support during this period of time.

Last but not least, we offer our deepest appreciation to our families on behalf of their heartfelt support and sacrifices that have propelled us to accomplish such an extraordinary feat.

Göteborg January 2012.

Arman Jamali

Christoffer Skantz

Nomenclature

BOD- Biological Oxygen Demand

COD- Chemical Oxygen Demand

CWT- Centralized Waste Treatment

DOC- Dissolved Organic Carbon

EBCT- Empty Bed Contact Time

EQS- Environmental Quality Standard

EUWFD- European Union Water Framework Directive

GAC- Granular Activated Carbon

PAC- Powder Activated Carbon

PSI- Pounds per square inch

SEPA- Swedish Environmental Protection Agency

TOC- Total Organic Carbon

TOT- N- Total Nitrogen

TOT- P- Total Phosphorus

USEPA- United States Environmental Protection Agency

UCL_{95}- 95 % Upper Confident Limit

WWTP- Waste Water Treatment Plant

1 Introduction

Contaminated leachate has been observed from the Välen mud deposit site which potentially has adverse effects on the nearby environment and especially on the Välen bay. Mercury is one of the most toxic metals known and occurs in the leachate in high concentrations among other heavy metals. There is hence enough motivation to conduct an extensive research to determine the leachate flow and suggest treatment techniques for remediate the contaminated leachate from this site.

The results from this study are going to be used as a basis for selection of a treatment technique for the mercury contaminated leachate water leaving the Välen mud deposit site located in Göteborg. The thesis is made in cooperation with Kretsloppskontoret, Göteborg stad because further treatment may be required to improve the water quality in Välen in line with the SEPA (Naturvårdsverket) restrictions.

1.1 Aim and goal of study

The aim of this study is to find an appropriate technique for treating the contaminated leachate water from the Välen mud deposit site with focus on mercury. Through assessments and comparisons of different possible techniques the most sustainable and appropriate application will be proposed to serve as the base for making a pilot/full scale treatment facility on site.

The specific goals of this study can be described as:

- Research of efficient techniques to treat mercury contaminated water and compare the treatment technologies based on certain criterion.
- Design and running of an activated carbon adsorption facility, a column system with two columns in series, in field for determination of the sorption material break-through and efficiency i. e. a practical pilot test.
- The flow is needed for design dimensions and in estimation of costs for the treatment facility.

1.2 Site description

The 5 hectare big Välen mud deposit is situated on the western shore of the Välen bay in height with *Åkered*, north of *Björla* port, see Figure 1.

Figure 1. The position of the Välen bay (upper Figure) and the Välen mud deposit site (lower Figure).

The mud deposit site was in use for a relatively short period, 1976-1977. The mud consists mainly of sludge sediments from the inner parts of *Askim* and *Välen* bay. The origin of this sludge is from the effluent water from *Näsets* WWTP (Waste Water Treatment Plant) that was running from 1953 until 1974. The remediation of the bay included an excavation of 30 000 m^3 sludge that was put on this site within 3 meter walls, 30 meters from the shore line and was covered with limed sludge from *Ryaverket* WWTP and topsoil. The wall prevents leachate of contaminated water to the surrounding area and the cover protects from infiltration of water into the deposit.

The area is considered as a valuable site for recreational and natural interests e.g. for swimming and recreational purposes. The ground beneath and adjacent to the deposit is to be considered as geotechnical instable. Aquifers or similar ground waters are missing in the vicinity of the deposit. The Välen bay has according to the municipality's risk assessment a high environmental value and is together with the *Askim* bay a productive shallow bay for fishing. Additionally the bank of the Välen bay including the reed areas have a strong interest for the bird life (Melica, 2010b).

1.3 Performed risk assessment and taken actions

On behalf of *Kretsloppskontoret*, Göteborgs stad, *Golder Associates* conducted a risk assessment 2004 to investigate the Välen mud deposit among 15 other landfills in Göteborg region that *Kretsloppskontore*t are responsible for. Since each individual object has its own special requirements that must be considered in its own way, *Golde*r developed a customized methodology to systematically assess the environmental and health risks and potential remediation measures. The risk assessment was carried out with the purpose to briefly compare the landfills with each other and the results could hopefully work as a basis for prioritizing further research and necessary action efforts for an economic risk analysis. The project did not include any field investigations; only some stereotype landfills were visited in order to obtain an idea of the landfill to the general appearance and character. No investigations were performed by *Golder* after September 2003, and the data obtained thereafter was not included in the risk assessment report (Associates, 2004).

The assessments made on information puts the Välen mud deposit into probability category C and in impact category 2, which results in the risk ranking 2 i.e. low to medium risk. The uncertainties are though set to be high. The risk ranking is summarized to be due to:

- Contaminated dredged material (mud).
- Protection worth area (recreation, nature conservation).
- Geotechnical unstable waste/area.
- Observed leachate from the site containing high values of e.g. heavy metals and macro nutrients.

The suggested mitigation measures for the Välen mud deposit site were the following:

- Internal relocation of waste – reducing surface.
- Additional dense coverage reduces leachate formation.
- Leachate ditches can be drawn (collection).
- A more in depth site investigation is needed.

Based on the risk assessment, environmental measures were conducted between Augusts to September 2005. The measures included; burial of a shield at a point where leachates had been observed, installation of sludge well and digging of a ditch in the southwest end of the deposit. The leachate is led through a drainage pipe to the shield that forces the water to the sludge well and discharged out to the bay via a pipe. A control program was also set up with the purpose to see the environmental impact from the deposit to the ambient water and ecology as well as to monitor and assess the efficiency of the performed environmental measures at the site (Melica, 2010a).

The control program includes measuring the concentrations of pollutants in the leachate water in the ditch (Y1), in the sludge well (L1) and in two ground water wells, Gv2 which is located within the deposit and Gv1 which is located in the south part of the wall. Measurements have been done in line with the control program since 2005 and the results show that several contaminants concentrations still exceeds the guideline values (Melica, 2010a). Analysis results can be seen in the Appendix 6.

1.4 Former measurements

The annual infiltration is estimated to be 250 mm/year which is equal to a formation of 12500 m^3 leachate water per year (Melica, 2010a). How much of the infiltrated water that enters to the drainage pipe and then to the sludge well was up to date unknown. Some amount of water is believed to go through or above the wall since measurements of contaminants concentrations in the ditch has shown being high (Melica, 2010a).The ditch has been dug to collect drained water from surrounding areas to avoid additional infiltration to the deposit, and to avoid surface run-off from the deposit to enter to the surroundings. The measurements of contaminants concentrations have been done from 2006 to 2010, and the results are presented in Appendix 6. All values have been compared to different guideline values such as Swedish EPA (SEPA), Canadian guideline value, for mercury (Hg) in filtered samples. The European Union Water Framework Directive (EUWFD) guideline values and Göteborg guideline values for Hg in discharge were added as well.

All measurements of TOC, COD, total N, total P and Ni show that the concentrations in leachate water are above SEPA guideline values during the whole time period and are most of the time extremely high. Mercury and especially methyl- mercury ($HgCH_3$) are another crucial element. Analysis results for mercury is presented as both filtered and unfiltered samples, where the unfiltered shows the total mercury including mercury bound to particles.

The guideline values most often used for total mercury (inorganic and organic mercury) are the Canadian; 0.1 µg/l (Gaudet, 1995) and the EUFWD; 0.05 µg/l (Zielonka, 2008). The concentrations of mercury in the former filtered samples were under the detection limit of 0.1 µg/l. Since the EUWFD guideline value is 0.05 µg/l, the concentrations may be over that guideline value even if reported as not detected. The unfiltered samples are often above the *extremely serious* concentration of 1 µg/l, according to the Canadian guideline values (Swedish EPA 2002). However, the guideline value for total mercury in this report refers to the Gothenburg value for point of discharge to recipients which is 0.07 µg/l (Carlsrud, 2008). This value is valid for both unfiltered and filtered samples while the Canadian guideline value and the EUFWD value are valid only for dissolved total mercury i.e.inorganic and organic mercury in dissolved forms. Methyl mercury (MeHg), should not exceed 10 ng/l for surface waters according to the Canadian guideline value (Gaudet, 1995).

Since there are no guideline values valid for unfiltered mercury, unfiltered samples will therefore also be compared to these guidelines but the concentrations are then expected to be higher than if they were filtered. This is the reason why filtered samples also will be analysed.

Other substances such as Arsenic (As), Chromium (Cr) and Copper (Cu) are exceeding the guideline values and may be considered as crucial elements. Lead (Pb) is considered to be a toxic element but it seems that its concentration in this case is not that high except during one measurement (October 2010) when the concentration was above the guideline value.

In the ditch (Y1), there are some critical concentrations of TOC, DOC, N-total and P-total which all are above guideline values. Ni and Pb exceeded the guideline values only at some occasions during (2008-2010). The concentration of total mercury (Hg) is half of the time below the guideline value, and half of the time at the moderately serious level. Methyl mercury (MeHg) is in some occasions above the guideline value.

Table 1. Evaluation of potential hazardous substances in the leachate from the sludge well (L1).

Substance	**Unit**	**Hazard classification** [5]	**UCL** $_{95}$ [6]	**Guideline value (filtered)**	**Guideline value (unfiltered)**[3]	**Potential hazard to Välen?**
TOC	mg/l	-	2710	< 4[1]	12	Yes
COD_{Mn}	mg/l	-	1041	< 4[1]		Yes
N-tot	mg/l	-	857	<0.3[1]	1.2	Yes
Ammonia	mg/l	Very Hazardous	502	_/0.5[2]	_	Yes
P - tot	mg/l	-	1.63	< 0.0125[1]	0.05	Yes
Al	mg/l	Moderately Hazardous	41.4	_ /0.5[2]	_	No
As	mg/l	Extremely Hazardous	0.014	<0.0004[1]	0.015	Yes
Cd	µg/l	Extremely Hazardous	0.27	<0.01[1]	0.3	Yes
Cr	mg/l	Very Hazardous	0.02	<0.0003[1]	0.015	Yes
Cu	mg/l	Very Hazardous	0.01	<0.0005[1]	0.009	Yes
Hg	µg/l	Extremely Hazardous	4.01	0.05[7]	0.07	Yes
MeHg	µg/l	Extremely Hazardous	216	0.01[4]	_	Yes
Na	mg/l	Extremely Hazardous	27.2	100 /_[2]	_	No
Ni	mg/l	Very Hazardous	0.5	<0.0007[1]	0.045	Yes
Pb	µg/l	Extremely Hazardous	1.93	<0.0002[1]	3	Yes
Zn	mg/l	Moderately Hazardous	0.02	<0.005[1]	0.03	Yes

1) SEPA guideline values for lakes and water courses (very low-low) (Swedish EPA, 2000)
2) Refers to guidelines from the National Board of Statutes for precautions for drinking water with unfit/fit. Unfit means a risk of health effects to humans if above the value. Fit means that it has a less satisfactory composition but no health effects for humans (Swedish EPA, 1999).
3) Gothenburg value for point of discharge to recipients (Carlsrud, 2008)
4) Canadian water quality guidelines for the protection of aquatic life (Gaudet, 1995).
5) SEPA- contaminated sites (Swedish EPA, 2002)

6) UCL_{95} (Upper Confidence Limit) is a numeric value based on the average value plus a standard error. It is based on a mixture of both unfiltered and filtered samples for all substances except for mercury.
7) European Union Framework Directive (Carlsrud, 2008)

Table 1 lists the most of the elements that has been analysed. Here is seen a classification of the elements from SEPA and concentrations given as the upper confident level with a 95 % certainty. This value has been calculated based on all former measurements and are with a high certainty the highest expected concentrations in the leachate water from the sludge well and can be seen as the worst case scenario. The UCL_{95} value is calculated as the average value of a sample population and adding the standard error which is dependent on the standard deviation, level of uncertainty (alpha value, in this case 5 %) and the number of samples. To see the full calculations see Appendix 6.

The guideline values for the same elements are presented and here the lowest level is selected to be on the safe side. As seen in Table 1, the UCL_{95} values are much higher than the guideline values and many of the elements are considered to be very or even extremely hazardous if occurring over the guideline values, hence the leachate contains hazardous contaminants that pose a risk on the Välen bay. The elements not included in Table 1 were either below the guideline value or not considered as hazardous according to SEPA. For the elements presented, mercury will be of high concern. This is mainly because methyl mercury is considered to be the most hazardous substance and since its UCL_{95} value occurs in the most relatively highest concentration in comparison with its guideline value (21600 times the guideline value).

The Välen deposit site could for these reasons be considered to be in need for additional mitigation measures in order to lower the concentrations of pollutants to decrease the impact to the Välen bay which today does not fully meets the requirements for “good status” in line with SEPA and EUWFD (Länsstyrelsen Västra Götalands län, 2009).

1.5 Scope and limitations

This thesis is supposed to investigate, based on a literature study, the possible techniques for treating mercury contaminated leachate waters. Due to the time limitation it is not possible to test all methods in reality i.e. to make neither pilot scale tests nor laboratory researches. Therefore assumptions and correlations will be done based on theoretically facts and existent pilot/full scale projects.

Methods for remediation of the soil/sludge will not be investigated since the site is a relatively large deposit site and not just a contaminated area where any planned projects is desired for recreation or residential purposes. Instead the focus is to treat the leachate that leaves the site and enters into the Välen bay.

The existing measures on site including the drainage pipes, sludge well and the screen will not further be investigated neither any site investigation. All possible methods are considered to be feasible onsite. The focus is on the collected water in the sludge well not considering water which goes to the ditch or to other parts within the area. The most proper treatment techniques will be estimated based on a comparison of different techniques. Parameters in the comparison part will be defined by the authors.

Among different pollutants in the leachate, the main focus is to lower the concentrations of mercury as mercury is a priority substance. The techniques will be evaluated on the basis of the capacity to treat primarily mercury. If the treatment technique seems to be efficient for mercury removal then the efficiency for removing other elements will be seen as positive.

Determination of the leachate flow to the sludge well is included in the study because it is needed for an assessment of treatment techniques. This operation is further described in chapter 2. A pilot test will also be done in field to see the potential in a treatment technique and is further described in the method section.

2 Methodology of thesis

A literature study will be conducted aiming to research about various treatment technologies for treating leachate containing mercury and other relevant pollutants similar to the leachate from the Välen mud deposit. A general introduction for various possible treatment techniques are presented in chapter 3. In order to be able to assess the applicability of a technique at the case study site Välen, some indicators should be defined. The needed parameters for this purpose are:

a) Cost (capital and annual O&M)
b) Mercury removal efficiency
c) Functionality
d) Eco-friendliness (materials and residues)
e) Social aspects

The site applicability of the various studied techniques will be evaluated in chapter 7 in this report. The information gathered from the litterature study will be estimated based on the leachate flow to the sludge well at Välen and the composition of the water. The outcome of the site specific part will be summeriesed in the chapter 8 and the chosen treatment tehniques will be compared in this chapter. The indicatorsare the ones stated above (a-e). Further information about the comparsion including score setting, see chapter 8. Depending on the results from the pilot experiment or the literature search suggestions will be given for any further necessary studies and is presented in chapter 9.

3 Theoretically introduction of treatment techniques

All techniques with a good efficiency for mercury removal will be described. A general description of the techniques and how to be operated are given. The technique must be proven to be efficient for mercury treatment. Economical information is also discussed.

3.1 Adsorption

Adsorption is one of the common techniques that are used for aqueous mercury treatment. This technology is considered either as a primary treatment method or a polishing step for further removal of mercury. The amount of contaminants adsorbed is an important characteristic which shows the adsorption capacity of an adsorbent (U.S. EPA, 2007). The adsorbent is often packed into a column, and mercury contaminated water is passed through the bed including different types of adsorbents which are able to adsorb various mercury compounds from the water. When the adsorption media is saturated, the adsorbent should be regenerated or disposed and replaced with new adsorbent. Heat or steam is sometimes used for desorption of contaminants for regeneration of adsorbent material (U.S EPA, 2000). The characteristics of contaminated water are important in terms of adsorption efficiency, and pre-treatment steps such as sulfide precipitation, filtration or pH adjustment may be done (U.S. EPA, 2007).

Activated carbon

Activated carbon are carbonized or activated in special processes, and the most common used materials are coal, wood, coconut shell or peat (U.S.ACE, 2001). The granular activated carbon (GAC) is predominantly used in adsorption processes (U.S EPA, 1997). Parameters as pore size distribution, surface area and surface chemistry affect the adsorption capacity (U.S. EPA, 2007). If the particle size decreases, the adsorption rate increases; the more uniform pore size distribution, the higher contaminant movement to the carbon surfaces.

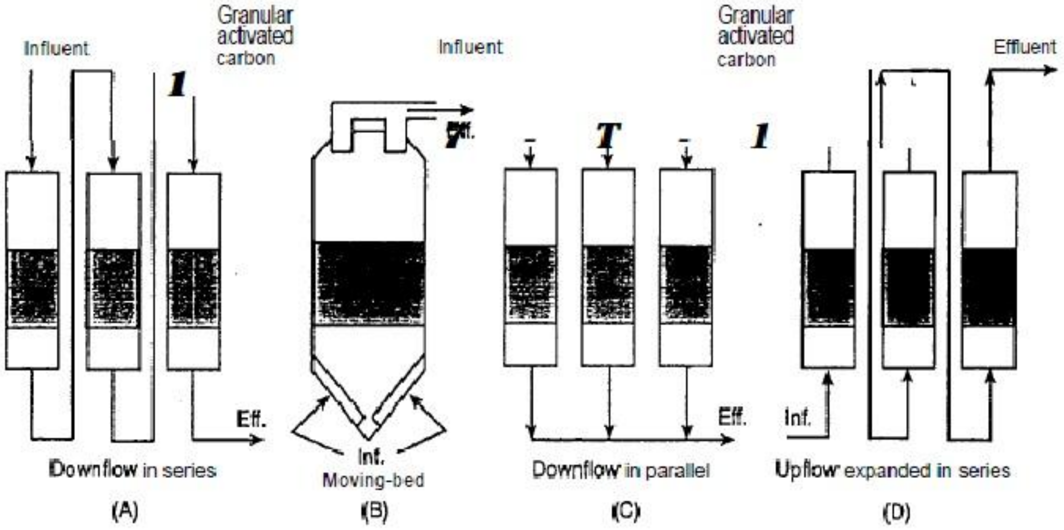


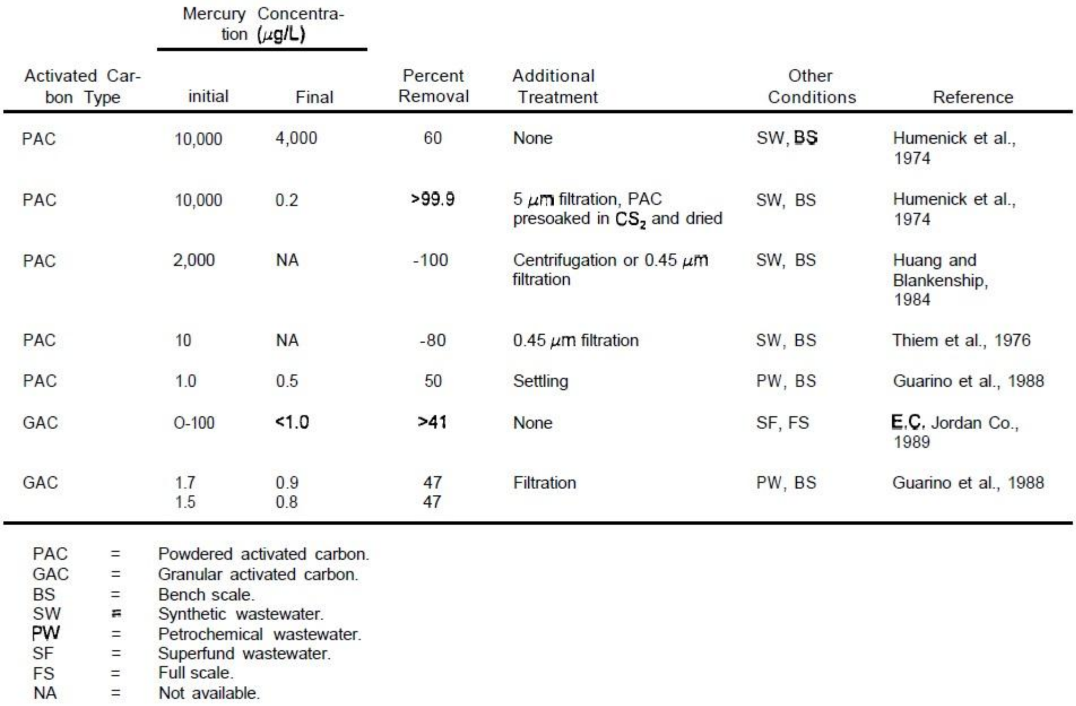
Figure 2. Types of GAC column design (U.S EPA, 1997).

There are different types of GAC column design which work based on pressure or gravity (U.S EPA, 1997), see Figure 2. The configurations could be columns in series or in parallel with up flow or down flow, expanded, packed or fixed carbon beds (U.S EPA, 1997). The GAC is found in different sizes for liquid treatment; the most common mesh size is 8×30 (2.36×0.60 mm) (U.S.ACE, 2001). Humenic and co-investigators (1974) showed that activated carbon impregnated with disulfide solution increases mercury removal from initial concentration of 10 mg/l to 0.2 µg/l. In this mechanism a chemical bond is formed between carbon disulfide molecules and mercury ions.

In a pilot plant study using F-400 GAC in two columns in series each of 30 min EBCT, 13.6 kg of GAC was used in each column with a flow rate around 0.95 l/m, the initial mercury concentration in average was 3800 µg/l. The breakthrough happened after treatment of 316 L of wastewater per kg of GAC (based on replacement of the adsorbent in two columns) reaching mercury concentration 20µg/l. The result showed 99.8% of mercury removal at the average pH around 8.3 (Cyr et al., 2002).

Powdered activated carbon (PAC) is made of small carbon particles (0.180 mm) (U.S.ACE, 2001). The PAC is generally added to different process units of contact reactor as a slurry or liquid (U.S EPA, 1997). Due to poor recovery and high headloss in the vessel, PAC is not commonly used (U.S EPA, 1997; U.S.ACE, 2001). According to Patterson et al., the achieved residual mercury concentration is 0.5 to 20 µg/l when activated carbon treatment is applied. Results of mercury treatment by activated carbon from different studies are presented in Table 2.

Table 2. Activated carbon mercury treatment results (U.S. EPA, 1997).



Activated Carbon Type	Mercury Concentration (μg/L) initial	Final	Percent Removal	Additional Treatment	Other Conditions	Reference
PAC	10,000	4,000	60	None	SW, BS	Humenick et al., 1974
PAC	10,000	0.2	>99.9	5 μm filtration, PAC presoaked in CS_2 and dried	SW, BS	Humenick et al., 1974
PAC	2,000	NA	-100	Centrifugation or 0.45 μm filtration	SW, BS	Huang and Blankenship, 1984
PAC	10	NA	-80	0.45 μm filtration	SW, BS	Thiem et al., 1976
PAC	1.0	0.5	50	Settling	PW, BS	Guarino et al., 1988
GAC	O-100	<1.0	>41	None	SF, FS	E.C. Jordan Co., 1989
GAC	1.7 1.5	0.9 0.8	47 47	Filtration	PW, BS	Guarino et al., 1988

PAC = Powdered activated carbon.
GAC = Granular activated carbon.
BS = Bench scale.
SW = Synthetic wastewater.
PW = Petrochemical wastewater.
SF = Superfund wastewater.
FS = Full scale.
NA = Not available.

Sphagnum Peat Moss

Peat is a type of plant containing decomposed organic materials which growths in humid places like wetlands. It’s usually a dark brown plant including lignin and cellulose as the main constituents. The polar characteristics and high percentage of pores besides being cheap and easy to use, has made peat as a suitable sorbent in the treatment of wastewater (Couillard, 1994).

Peat can sorb most metals up to 4% of its dry weight. The maximum adsorption capacity of peat moss for Hg achieved in a batch system study was 82 mg/g. The equilibrium concentration for mercury was obtained at 49 mg/l (Bulgariu, 2008). The equilibrium time of mercury sorption onto peat based on two studies differs from 5 h using raw wastewater (Virarghavan, 1995) and 30 min using a solution of mercury ions (Lalancette, 1972). The optimum pH for mercury treatment ranging from 5 to 5.5.

Assessing mercury sorption onto peat at different temperatures showed that the Langmuir constant (adsorption/desorption energy) in comparison with Cu, Ni and Zn increased somewhat as the temperature increased. It might be an endothermic reaction, because the interaction between sorbent and sorbate is increased in higher temperature (Virarghavan, 1995). The Freundlich constant (shows the sorption capacity) increases as the temperature increases (Bulgariu, 2008).

Incineration and landfill are two ways of disposal of spent peat (Coupal and Lalancette, 1976). Although for most of the metals acid washing is a proper method for removing metals (Gosset et al., 1986). Loading rates of metals in the wastewater is an important factor influencing sorption. The lower loading rates the higher sorption efficiency (Brown et al., 2000).

Peat has low hydraulic loading rate about 1.5-84 cm^3/cm^2-day which proves that it might not be suitable for a high flow rate of wastewater to the system. One important advantage of this system is their low capital and operational cost (Couillard, 1994). The peat treatment system sometimes faces to a number of problems. Clogging in the peat system happens sometimes due to presence of small particles in the peat bed which causes the reduction of hydraulic charge in the treatment system. The yellow-brown colored effluent of peat might affect the aesthetic of the effluent of the system (Buelna, 1993).

The cost of adsorption techniques

The cost of using granular activated carbon for removing thimerosal (a mercury salicylate salt for stopping the growth of bacteria and fungi) in a pilot plan study was 0.7 SEK per 3.8 L of water. It means the capital cost and operation and maintenance cost of this project were 0.076 SEK and 0.61 SEK per 3.8 L of water, respectively. The treatment costs reported for a full scale project of thimerosal removing were 384,000 SEK and $50,000 for the capital cost and monthly operating, respectively, for treatment of 6.8 L of wastewater per day. In other words, the annual operating cost for treating 1971000 L/year of wastewater would be 588,000 SEK and this in turn would be 0.26 SEK/L.

Two different prices of peat were available for authors. The first one is 140 SEK/m^3 (personal communication) and the other one (based on 1999 U.S dollar) is 170 SEK/ton ($26.48) (Jasinski, 1999).

3.2 Precipitation/Co-precipitation

Precipitation/co-precipitation is a common technology for treatment of heavy metals-contaminated wastewater or leachate (U.S. EPA, 2007). The mercury concentration can be reduced to less than 2 µg/l by this method. Sometimes in order to reach the optimum level of concentrations, other additional treatments are used. Adjustment of pH and flocculation are examples of additional processes which can be followed by solid separation such as gravity settling and/or polishing as filtration method. This method comprises addition of chemicals to the contaminated water, formation of solid particles via precipitation and in the final step, separation of solid particles from water. The schematic model of precipitation/co-precipitation is seen in Figure 3.

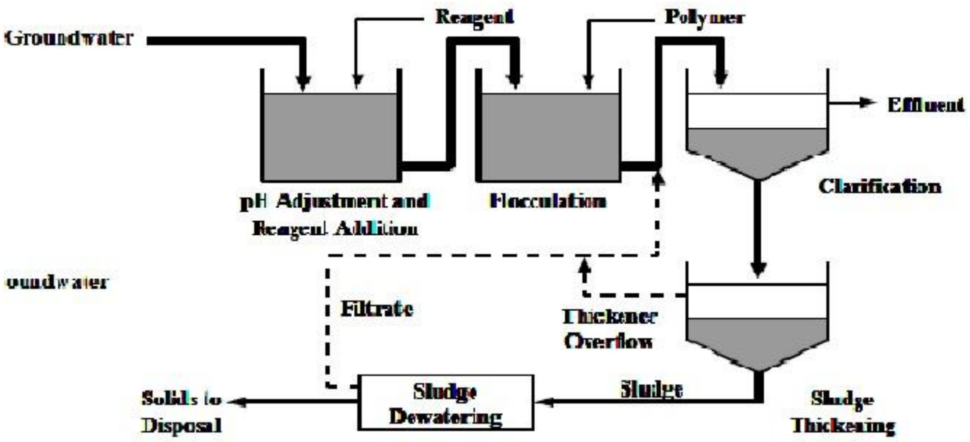


Figure 3. Schematic model of precipitation and co-precipitation (U.S E P A, 2002).

Ferric salts such as ferric chloride, aluminium, pH adjustment, lime softening, sulfide and lignin derivatives could be used for precipitation (U.S. EPA, 2007). The sludge from mercury treatment can be hazardous and should be treated via stabilization and solidification and then disposal as hazardous waste.

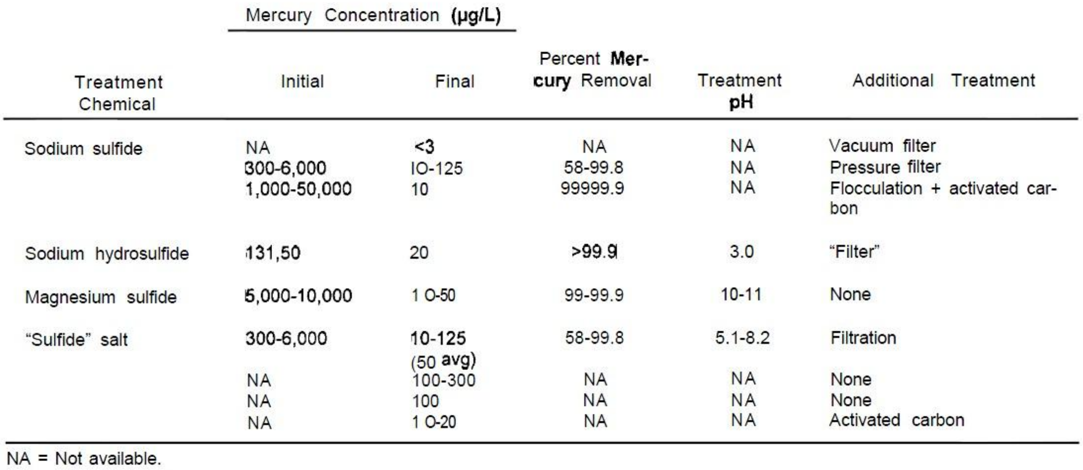
Sulfide precipitation

Sulfide precipitation is the most common precipitation method for removal of inorganic mercury from wastewater which is done through this reaction (U.S. EPA, 1997):

$Hg^{2+} + S^{2-} \leftrightarrow HgS_{(s)}$

The pH range is 7–9 and the sodium sulfide is mostly used as precipitant salt. The precipitated particles can be removed through gravity settling in a clarifier. Using over dosage of sulfide can cause the risk of the formation of soluble mercury sulfide. Sludge containing mercury can be a potential hazard when mercury is resolubilized under landfill condition (Hansen, 1992) which in turn causing mercury release to the leachate discharging out. In some cases, the effluent from precipitation may need additional treatment as pH adjustment before discharge (U.S. EPA, 2007). According to different researches, 99.9 % mercury removal is achievable from initial concentration more than 10 mg/l which is possible to even decrease the concentration to 10-100 µg/l by polishing treatment such as filtration (U.S. EPA, 1997). In pH above 9, the removal efficiency is reduced considerably. This method is mostly used for wastewaters from chlor-alkali plants. Table 3 shows the results of sulfide precipitation treatment for mercury.

Table 3. Sulfide precipitation for mercury treatment (After Patterson, 1985;U.S. EPA, 1997).



Treatment Chemical	Mercury Concentration (µg/L) Initial	Final	Percent Mercury Removal	Treatment pH	Additional Treatment
Sodium sulfide	NA	<3	NA	NA	Vacuum filter
	300-6,000	IO-125	58-99.8	NA	Pressure filter
	1,000-50,000	10	99999.9	NA	Flocculation + activated carbon
Sodium hydrosulfide	131,50	20	>99.9	3.0	"Filter"
Magnesium sulfide	5,000-10,000	1 O-50	99-99.9	10-11	None
"Sulfide" salt	300-6,000	10-125 (50 avg)	58-99.8	5.1-8.2	Filtration
	NA	100-300	NA	NA	None
	NA	100	NA	NA	None
	NA	1 O-20	NA	NA	Activated carbon

NA = Not available.

The cost of applying the sulfide precipitation for the chlor-alkali wastewater was reported as 5 SEK/3800 L (1000 gallon, $1987 basis) without considering the sludge management costs (U.S. EPA, 1997). According to Perry (1974), the capital cost (1995 basis) of using sulfide precipitation together with diatomaceous earth filtration for treatment of 380 L/min flow of chlor-alkali wastewater was reported as $2767.47/3800 L/day capacity. For assessment of the sulfide process, sludge management is an important factor in case of costs and environmentally friendly ways of disposing. The general drawbacks of this method are:

1. Resolubization of mercury from mercury-sulfide particles in high dosage of sulfide.
2. The problematic monitoring of real-time of reactor sulfide level.
3. The risk of toxic residuals sulfide in the effluent.
4. Tough clarification and sludge processing.
5. Disposing of sulfide sludge.

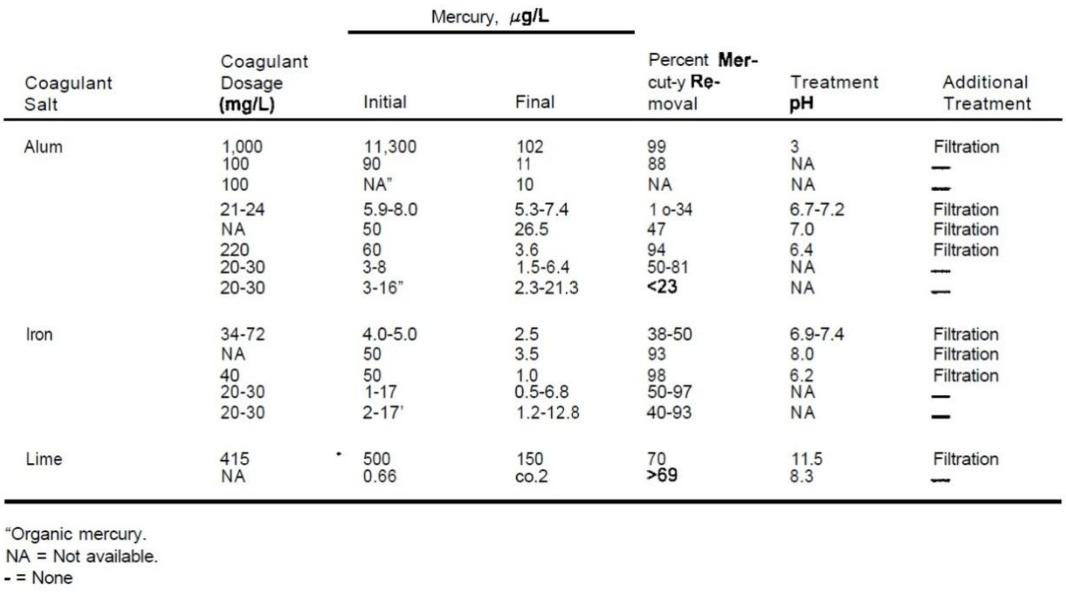
Coagulation/co-precipitation

The coagulants which are commonly used are aluminium sulfate (alum), iron salts and lime (U.S. EPA, 1997). Adsorptive co-precipitation is the best mechanism when alum and iron are used as coagulants (Patterson, 1992). In this mechanism, ion is adsorbed to a solid particle (bulk solid). As a further explanation, when alum is added, aluminium hydroxide is precipitated and the same process for iron. By addition of iron salts (ferric or ferrous), iron hydroxide is precipitated (U.S. EPA, 1997).

Increase in the formation of proper bulk solid will strengthen the treatment performance. Furthermore, adequate pH adjustment regulates bulk solid surface change and soluble mercury formation (U.S. EPA, 1997). Through some treatments of inorganic mercury following filtration, 94% to 98% removal efficiency was achieved from initial concentration of 50 to 60 µg/l. The result for lime coagulation treatment following filtration was 70% removal from higher initial concentration of 500 µg/l (Patterson, 1985). Treatment results from coagulation/co-precipitation are presented in

Table 4. The final concentrations by applying alum are variable from 1.5 to 102 µg/l and normally from 5 to 10 µg/l while the values from iron treatment in a range from 0.5 to 12.8 µg/l (U.S. EPA, 1997).

Table 4. Mercury treatment results by coagulation/co-precipitation method (After Patterson, 1985;U.S. EPA, 1997).



		Mercury, µg/L				
Coagulant Salt	Coagulant Dosage (mg/L)	Initial	Final	Percent Mer-cut-y Re-moval	Treatment pH	Additional Treatment
Alum	1,000	11,300	102	99	3	Filtration
	100	90	11	88	NA	—
	100	NA"	10	NA	NA	—
	21-24	5.9-8.0	5.3-7.4	1 o-34	6.7-7.2	Filtration
	NA	50	26.5	47	7.0	Filtration
	220	60	3.6	94	6.4	Filtration
	20-30	3-8	1.5-6.4	50-81	NA	—
	20-30	3-16"	2.3-21.3	<23	NA	—
Iron	34-72	4.0-5.0	2.5	38-50	6.9-7.4	Filtration
	NA	50	3.5	93	8.0	Filtration
	40	50	1.0	98	6.2	Filtration
	20-30	1-17	0.5-6.8	50-97	NA	—
	20-30	2-17'	1.2-12.8	40-93	NA	—
Lime	415	500	150	70	11.5	Filtration
	NA	0.66	co.2	>69	8.3	—

"Organic mercury.
NA = Not available.
- = None

In a full scale project of treatment of contaminated groundwater from 1997 to 1999 at Marine Corps Base Camp Lejeune in North Carolina, the P&T (pump and treat) system was used to remove 41,000 pounds (18.6 ton) of contaminants including mercury. The P&T system comprised multiple treatment steps such as oxidation of ferrous iron, pH adjustment, precipitation, air stripping and GAC adsorption. The unit cost of this project was 320 SEK per 0.45 kg (1pound) of pollutant removed. The capital cost and the annual cost of the operation and maintenance was 30,000,000 SEK and 640,000 SEK, respectively. The all costs are in 2000 US dollar (U.S. EPA, 2007). There is no available data for precipitation/co-precipitation process alone.

The land requirements and cost plus energy usage were estimated by U.S. EPA, 2000. The land requirement comprises total area for equipment and ancillary stuff (pumps, etc) plus 20 foot perimeter around each unit. The land requirement is multiplied by corresponding land cost and then the treatment facility land cost is estimated. Electricity, lighting and control are categorized as energy usage. The required electricity for treating 3800L (1000 gallons) of wastewater is 0.5 Kwh. Lighting and control cost 6,400 SEK/year and electricity 0.5 SEK per Kwh (U.S E P A, 2000).

3.3 Ion exchange and inorganic adsorption

Ion exchange is a reversible chemical reaction wherein ions from a solution are exchanged for similarly charged ions attached to a fixed solid particle. The ion exchange can take place at the surface of naturally occurring inorganic materials e.g. zeolites or by synthetically produced organic resins, where the latter are the predominant type used today due to that their characteristics can be tailored to specific applications.

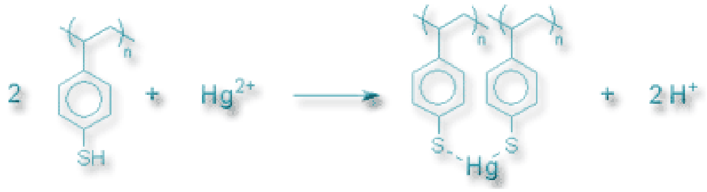
The advantages of reversible reactions is enhanced during regeneration of the resins when a solution containing the initial exchangeable ions attached on the resin is put in contact with the saturated resin to re-exchange the ions.

There are different kinds of resins, but the focus in this report is on one kind of resins, the so called chelating resins that forms chelates with cations and anionic complexes in the water. These are most often also selective for various substances e.g. mercury.

Chelating resins are insoluble polymers to which is attached a complex group or groups. These groups can bind metal cations within the structure so as to form a ring (or chelate) into which the metal is integrated (U.S. EPA, 1997). These resins have a high selectivity for heavy metals such as mercury and other precious metals and the resin type is often made of macro porous polystyrene cross linked with divinyl benzene (DVB) and functional groups are attached on the polymer chains (U.S. EPA, 1997). These groups can be e.g. thiol, thiouronium, amine or sulphur (Klasson, 1998a).

The functional group of a thiol is a sulfhydryl (-SH) which often is referred to as a mercaptan, which simply means “mercury capture” due to its good preference and ability to bind mercury. A thiol is any compound containing the sulfhydryl (-SH) bonded to a sp^3 hybridized carbon (Brown, 2009). Besides a good selectivity for mercury thiol has a strong tendency to bind certain other metal ions such as copper, silver, cadmium, and lead (U.S. EPA, 1997). Below is an example of how mercury is chelated by thiol:

$$2C_6H_5SH + Hg^{2+} \rightarrow (C_6H_5S)_2Hg + 2H^+$$



Two resins that due to various comparative experiments of resins has been proven to be relatively good sorption materials for mercury are SIR-200 from Resintech and Amberlite GT-73from Rohm & Haas, both having thiol as a functional group where the sulfhydryl is attached next to an aromatic ring (Fondeur 2002). Thiouronium (RCH4-S-C-N2H3) as a functional group (e.g. Purolite S920) is highly selective for mercury and other precious heavy metals with chelating properties (Purolite Company, 2010), but is actually not a true chelating resin since it does not form chelates as e.g. thiols.

The mercury is strongly complexed by the sulphur and nitrogen groups in the thiouronium and the whole mercury salt is incorporated on the resin (Purolite Company, 2010).

There is an order of selectivity (preference) exhibited by the resin. If a resin has a preference for mercury 2000 times that for calcium, then this means that if a solution contains equal molar concentrations of mercury and calcium, the resin will after use contain 2000 times more mercury than calcium (U.S. EPA, 1997)

Operation of Ion exchange

To develop an effective ion exchange system for contaminated water can be difficult because of the complexity of the water to be treated. Metals in waste water can exist as cations or complexed anions, be monovalent or polyvalent or may not exist as ions but bond to particulate matter (Galletti, 2007). Another problem with waste water is the presence of oxidizing agents, oils, greases and detergents that can harm the ion exchange resins. These substances should be removed upstream any ion exchange system. Some important information about wastewater chemistry according to Galletti (2007) is to know physical properties like pH and temperature, total solids and the presence of oxidants and complexing agents.

Ion exchange columns operate on a similar service cycle as adsorption e.g. activated carbon columns, and consists of six steps: (1) operation/exhaustion, (2) backwash, (3) regeneration, (4) slow rinse, (5) fast rinse and (6) return to service. A simple single column system is possible but more commonly a multi-column process is used either in parallel or in series (Clifford, 1999). When operating in series the first one is regenerated when fully exhausted and the polishing column is partially exhausted (effluent exceeds the Maximum Concentration Limit “MCL”). The newly regenerated column now becomes the polishing column, see Figure 4 (Clifford, 1999).

In this way the risk of exceeding the MCL is decreased during the regeneration step. Another option is to operate in parallel. The advantages of this is that it can “smooth out” peaks during overruns and a variability in inlet concentrations and flows. The columns can also operate at different stages of exhaustion, and the effluent water is blended to have a more constant effluent concentration (Clifford, 1999).

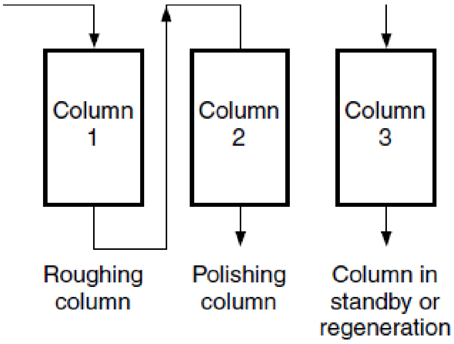


Figure 4. A merry-go-round approach with one column out of operation (Clifford, 1999).

The regeneration can be done either co-current (downwards) or counter current (upwards). According to Clifford 1999, both modes have their advantages and drawbacks. The regeneration process in different modes is fully described by Clifford (1999).

Resin characteristics

When knowing what kind of resin to be used it is good to know the total capacity but if possible, the operating capacity is more proper since it describes the actual performance of the resin under a defined set of conditions including feed water composition, service flow rate and degree of regeneration (Clifford, 1999). The operating capacity is however only obtained after experiments with the true conditions and can hence not be determined prior to a test.

The total capacity of a sorbent is often expressed in mass equivalents per unit volume of resin (eq/l). An equivalent is the molecular weight expressed in grams of the desired compound divided by its electrical charge or valence (engineering). As an example, a resin with a mercury removal capacity of 1 eq/L could remove 100 g of divalent mercury per liter of resin, (molecular weight of 200 divided by 2).

Chelating resins that often has an order of selectivity are given the capacity for a particular substance. It is good to know also the capacity for other competitive elements in the feed water that also has a relatively high preference by the resin.

Bed size and flow rates

The bed volume of resin needed is determined by the Empty Bed Contact time (EBCT) as in the case of adsorption beds. Seen often in literature is a recommended Service Flow Rate (SFR) which is the reciprocal to EBCT, see equation [1] and is most often expressed in bed volumes per time e.g. (BV/min). The reason for expressing the flow rate in (BV/min) is to let the results be independent on the column size (Hollermann, 1999).

$$ServiceFlowRate\,(SFR) = \frac{1}{EBCT} = \frac{Q}{V}$$

Where V is the resin bulk volume (including voids) and Q is the volumetric flow rate.

To design an ion exchange column system is similar to that of adsorption columns e.g. activated carbon and the following steps are vital according to (Clifford, 1999):

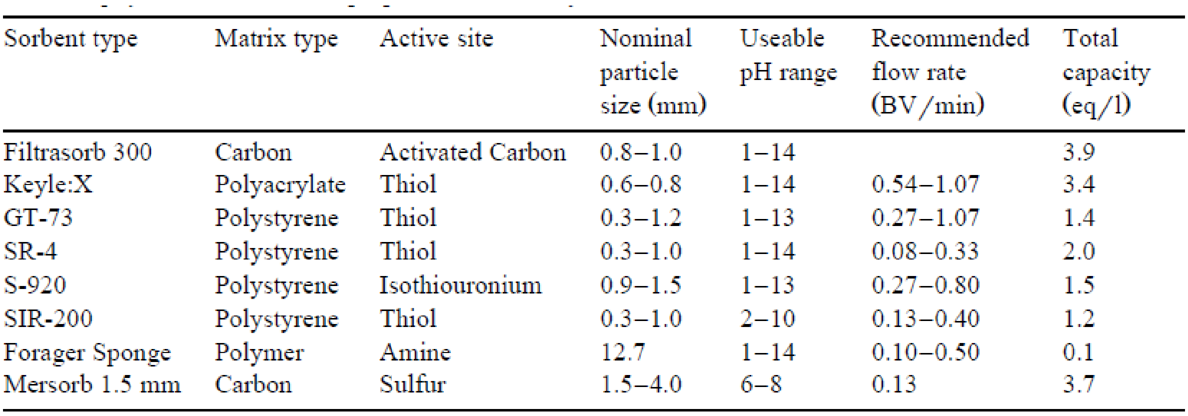
1. Select a proper resin, regenerant (if any suggested) and the level of regenerant from the resin manufacturer’s literature.
2. If bypass of water is suggested or needed, determine the allowable fraction of bypass source water.
3. Select the proper SFR or EBCT.
4. Calculate run length and the bed volumes that can be treated before breakthrough.
5. Calculate the volume of resin required.
6. Determine the minimum “out-of-service” time during the complete regeneration (hours).
7. Choose the number of columns and column system (series, parallel, single column?).
8. Dimension the columns.

9. Calculate the volume and composition of wastewater to be taken care of/disposed of.

Chelating resin study

A column test was conducted with the purpose to reduce mercury down to trace- levels. In the test various chelating resins were tested. These were compared to other materials potential to reduce mercury. Table 5 shows these materials properties. SIR- 200, Keyle:X and GT-73 showed the best results. For information about the various chelating resins included in that study, see Appendix 1.

Table 5. Mercury sorbent materials used in the test with some of their physical and chemical properties (Hollermann, 1999).



Sorbent type	Matrix type	Active site	Nominal particle size (mm)	Useable pH range	Recommended flow rate (BV/min)	Total capacity (eq/l)
Filtrasorb 300	Carbon	Activated Carbon	0.8–1.0	1–14		3.9
Keyle:X	Polyacrylate	Thiol	0.6–0.8	1–14	0.54–1.07	3.4
GT-73	Polystyrene	Thiol	0.3–1.2	1–13	0.27–1.07	1.4
SR-4	Polystyrene	Thiol	0.3–1.0	1–14	0.08–0.33	2.0
S-920	Polystyrene	Isothiouronium	0.9–1.5	1–13	0.27–0.80	1.5
SIR-200	Polystyrene	Thiol	0.3–1.0	2–10	0.13–0.40	1.2
Forager Sponge	Polymer	Amine	12.7	1–14	0.10–0.50	0.1
Mersorb 1.5 mm	Carbon	Sulfur	1.5–4.0	6–8	0.13	3.7

Initially a short- term test was conducted aiming at determine the maximum flow rate (Bed volumes/min) that could pass through the sorbents to achieve the effluent target concentration which is 51 ng/l (Hollermann, 1999; Klasson, 1998b).

Figure 5 shows the effluent concentration compared to the effluent limit for some of the sorbents for various flow rates. SIR-200 showed the best results and reduced the mercury below the level of 51 ng/l during flow rates under 3.0 BV/min. This shows that the SIR- 200 removed mercury at higher flow rates than recommended as seen in Table 5 namely 0.13- 0.40 BV/min.

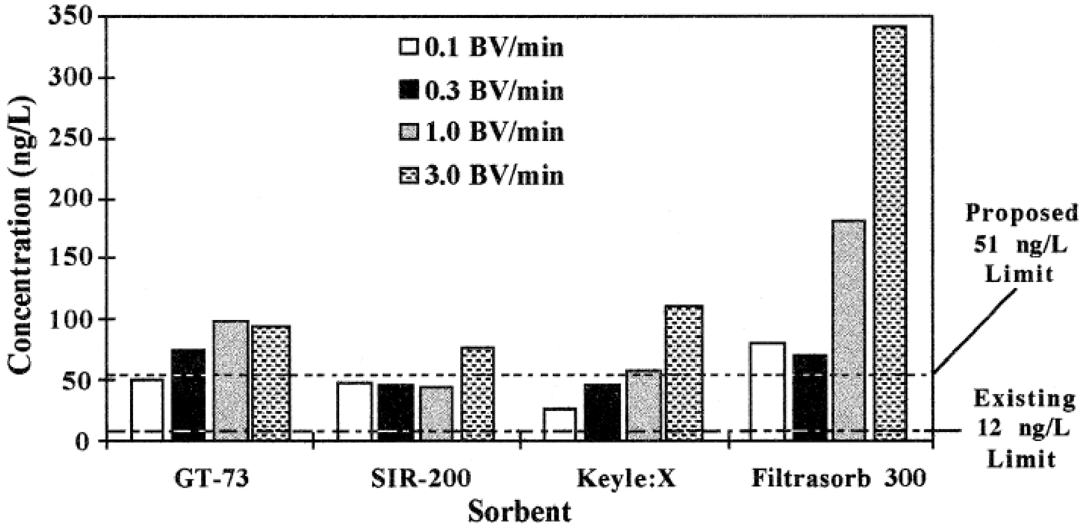


Figure 5. Achieved mercury effluent concentrations for some sorbents for various flow rates (Hollermann, 1999).

For Keyle:X the removal efficiency was as good as 96.7 % for a SFR of 0.1 BV/min as seen in Figure 5. At a SFR of 1.0 BV/min which is higher than the lowest recommended for Keyle:X, the removal efficiency was 93.5 %.

Keyle:X, SIR-200 and SAMMS were tested also in a long term test (Klasson, 1998b). The SFR was 1 BV/min and the same columns as in the short- term test were used (Klasson, 1998b). The results are shown in Figure 6.

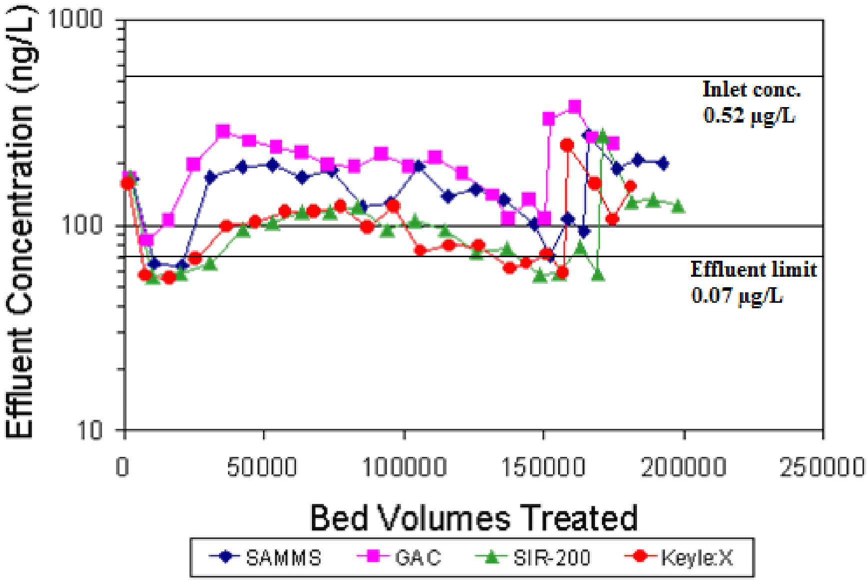


Figure 6. Long-term test of SAMMS, SIR-200 and Keyle:X compared with GAC (Filtrasorb 300). A flow rate of 1 BV/min was used and the incoming concentration was 520±195 ng/l.

Again SIR-200 and Keyle:X showed the best results. An effluent concentration of 60 ng/L was reached a couple of times, see Figure 6. With an average incoming concentration of 520 ng/L this means a reduction of 90 %. Making an average value of the effluent values obtained after Keyle:X and SIR-200 (about 100 ng/l) an average reduction of 80 % is reached. This is obtained with only one column and a relatively short contact time of 1 minute. With a longer contact time e.g. 7.7 min (0.13 BV/min), which is the longest recommended by the manufacturer for SIR-200, an even better result is likely. If looking at Figure 6, it seems like a breakthrough never occurs during this time of operation which means that the materials not are saturated.

3.4 Biological treatment

Phytoremediation (Biological treatment by plants)

Phytoremediation uses plants to remove, transfer, stabilize, or destroy contaminants in soil, sediment, and groundwater (U.S. EPA, 2007) . Phytoremediation is a generic term for several ways (biological, chemical, and physical processes) when plants crackdown contaminated substances. There are different phytoremediation mechanisms that plants exhibit for metal accumulation through hyper accumulation which are e.g. phytoextraction/rhizofiltration, phytostabilisation and phytovolatilisation.

However, in the case of very toxic compounds that occurs in high concentrations, the plants' natural capacity to hyper accumulate these substances is often not enough to clean contaminated sites or waters (Rugh, 2001). Plants can be genetically engineered to enhance their ability to absorb specific metals. By integrating bacterial resistant genes the plants can tolerate and remediate a specific toxic substance. In case of mercury, the mercury- resistant genes are inserted into plants that makes them highly tolerable to elevated mercury concentrations (Rugh, 2001; Nagata, 2010).

In a report from (Dhankher, 2003) *merA* and *merB* genes from the well-characterized bacterial *mer*operon were inserted into plants in order to engineer a mercury transformation system. The plants used were *Arabidopsis thaliana* and tobacco plants.

The bacterial *merB and merA* genes encodes for lyase and reductase that converts organic mercury like methyl mercury into organic molecules and cationic mercury into elemental mercury respectively within the cells. This makes bacteria or in this cases the plants more tolerant to mercury and much more efficient in converting harmful mercury into less harmful elemental mercury through volatilization.

There is one drawback to modify plants with only *merA* and *merB* together. This is because the plants volatizes elemental mercury into the surrounding environment. Since this has been concerned by the public further research in this field has been needed (Nagata, 2010). Released Hg^0 in the air can be inhaled and is inside the body transformed to Hg^{2+} which then also makes it harmful to living creatures (Rugh, 2001). Instead of modify a plant with both *merA* and *merB (*Nagata, 2010*)* inserted only the *merB* gene but also polyphosphate that can chelate the Hg^{2+} in the plant tissues. To increase the mercury uptake by the plant a bacterial *mer T* was also incorporated. The resulting *ppk/mer-T/mer-B* transgenic tobacco plant could absorb both organic and inorganic mercury at highly contaminated mediums and letting the Hg^{2+} be kept in the plant tissue without any Hg^0 release (Nagata, 2010).

Although several studies show that phytoremediation of mercury is possible, further research and pilot-scale studies will be needed to assess the effectiveness of the technology at full scale. A full-scale implementation need to consider several issues such as disposal of contaminated plants or the impacts of volatilized mercury on other ecosystems plants (U.S. EPA, 2007). Phytoremediation is limited to the root system of the plants. The root system must be deep enough to be able to take up the contaminants. Thus, having a contaminated site with contaminants deep down in the soil makes phytoremediation very limited (U.S EPA, 2000).

The Operation and Maintenance "O&M" of phytoremediation is fairly easy in comparison to other conventional techniques but there are a variety of steps that must be carefully considered before applying this method on a contaminated site as outlined by (U.S EPA, 2000). Among these the most crucial are the choice of plants, the distribution and type of contaminants and the physical parameters at the site like temperature, pH and water content.

The cost for phytoremediation depends on the characteristics of the soil and the choice of phytoremediation method and type of plants. The price also increases if harvest and disposal is required. In case of ordinary hyper accumulating procedure such as volatilization or genetically engineered plants with both *merA* and *merB* no harvest is required since the metals are transformed and volatized. If the metals are accumulated in the tissue, harvest is required and must be disposed of as hazardous waste. The cost for phytoremediation in general has been roughly estimated by US. EPA (2000) and for remediation of metals by phytoextraction the cost is about $200 000 for 12 acres (4.8 hectares) for a 30 year period. Simply dividing with 30, a yearly total cost (capital + O&M) is $6700. For phytostabilization a price of $1 per cubic meter of soil is estimated, though more uncertain whether it is the yearly cost and refers to the total cost. Removal efficiencies in studies or in generic terms have not been found.

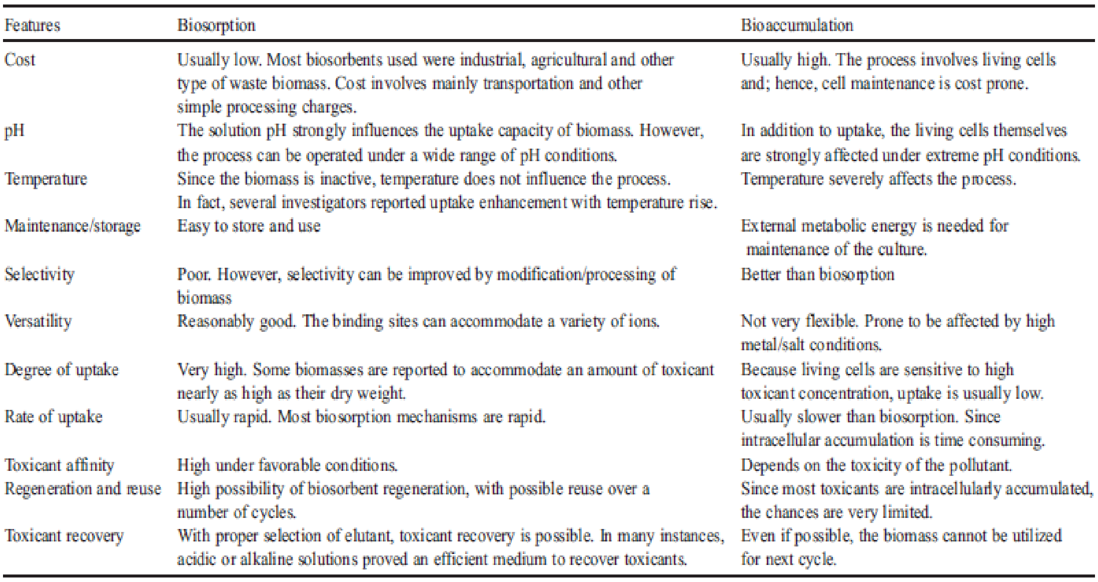
Bioaccumulation and biosorption

Microorganisms can detoxify and remove metals from waters by specific interactions including metal binding to microbial cell surfaces and exopolymer layers, intracellular uptake, metal volatilization and metal precipitation (Maier, 2009). Microorganisms e.g. bacteria can be used in constructed wetlands or to forming biofilms on various supports e.g. bio carriers, rotary drums or trickling filters, where the most common technique is the use of bacteria biofilms which may be viable (bioaccumulation) or nonviable (biosorption on biomass) (Maier, 2009). Bioaccumulation is defined as the uptake of toxicants by living cells, where the toxicants can be transported into the cell, accumulated intracellularly, across the cell membrane and through cell metabolic cycle (Vijayaraghavan, 2008). Biosorption is defined as the passive uptake by dead/inactive biological materials or microorganisms. Here the sorption is due to a number of metabolism- independent processes that takes place in the cell wall (Vijayaraghavan, 2008).

Often a mixture of biofilm- producing bacteria is grown on the support material in order to remove a variety of different metals. When viable microbial biofilms are used the biofilm rarely needs to be replaced but the bacteria require a proper environment to grow and to be efficient. Biomass however needs to be replaced since the removal efficiency will decrease with time. Since biomass is nonliving microorganisms they do not require the same maintained conditions (Maier, 2009).

The site specific conditions will determine whether biosorption or bioaccumulation is the best choice at a particular site. Table 6 below lists some parameters for comparison between Biosorption and bioaccumulation.

Table 6. A comparison of some parameters for biosorption and bioaccumulation (Vijayaraghavan, 2008).



Features	Biosorption	Bioaccumulation
Cost	Usually low. Most biosorbents used were industrial, agricultural and other type of waste biomass. Cost involves mainly transportation and other simple processing charges.	Usually high. The process involves living cells and; hence, cell maintenance is cost prone.
pH	The solution pH strongly influences the uptake capacity of biomass. However, the process can be operated under a wide range of pH conditions.	In addition to uptake, the living cells themselves are strongly affected under extreme pH conditions.
Temperature	Since the biomass is inactive, temperature does not influence the process. In fact, several investigators reported uptake enhancement with temperature rise.	Temperature severely affects the process.
Maintenance/storage	Easy to store and use	External metabolic energy is needed for maintenance of the culture.
Selectivity	Poor. However, selectivity can be improved by modification/processing of biomass	Better than biosorption
Versatility	Reasonably good. The binding sites can accommodate a variety of ions.	Not very flexible. Prone to be affected by high metal/salt conditions.
Degree of uptake	Very high. Some biomasses are reported to accommodate an amount of toxicant nearly as high as their dry weight.	Because living cells are sensitive to high toxicant concentration, uptake is usually low.
Rate of uptake	Usually rapid. Most biosorption mechanisms are rapid.	Usually slower than biosorption. Since intracellular accumulation is time consuming.
Toxicant affinity	High under favorable conditions.	Depends on the toxicity of the pollutant.
Regeneration and reuse	High possibility of biosorbent regeneration, with possible reuse over a number of cycles.	Since most toxicants are intracellularly accumulated, the chances are very limited.
Toxicant recovery	With proper selection of elutant, toxicant recovery is possible. In many instances, acidic or alkaline solutions proved an efficient medium to recover toxicants.	Even if possible, the biomass cannot be utilized for next cycle.

Biosorption

Bacillus sp. as nonliving biomass has shown to effectively bind heavy metals such as: mercury, cadmium, nickel, chromium and cupper among other metals (Maier, 2009). A study on Hg^{2+} removal by nonliving *Bacillus* sp. was done by (Green- Ruiz, 2005). The highest removal of 91.9 % was reached for an initial concentration of 0.250 mg/L of Hg (Green- Ruiz, 2005). Most of the mercury sorption occurred during the first 20 minutes and the saturation level occurred after 40 minutes for an Hg concentration of 1 mg/L and after 60 minutes for an Hg concentration of both 5 and 10 mg/L.

A pH interval of 3 – 9 was tested where 6 showed the overall best Hg removal. The pH seemed to have a greater influence on the sorption capacity for lower initial Hg concentrations.

Bioaccumulation

It is well known that naturally occurring bacteria, that are resistant against heavy metals, exist which has been analyzed in various experiments (Döbler, 2000). These bacteria can live in heavy metal rich environments since they can transform the metals intracellular. In the case of mercury both organic and inorganic mercury can be transformed by mercury reducing cytoplasmic enzymes encoded by the *merA* and *merB* genes in the *mer* operon in their cells see Figure 7 (Döbler, 2000). Various different bacteria with similar properties has been found and studied and some of them are in depth analyzed with their genome saved in databanks (Pepi, 2011). One drawback with the most mercury- resistant bacteria is that they volatize the elemental mercury back to the environment. There is hence desired to find bacteria that can efficiently remediate mercury without releasing it.

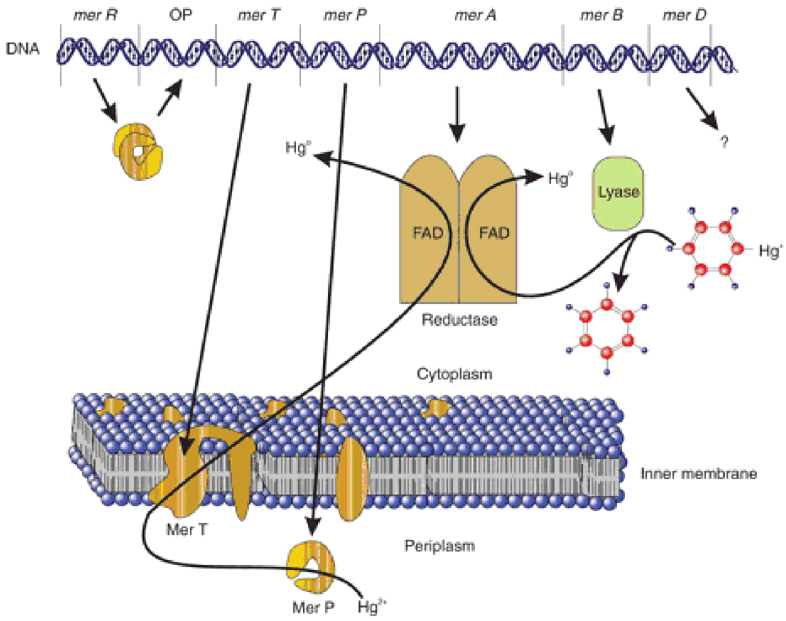


Figure 7. A model of bacterial mercury resistance encoded by the mer operon,(Maier, 2009).

In another study with the same objective by (Döbler, 2000) mercury- resistant bacteria (7 different strains of *Pseudomonas*) was kept in a bioreactor to treat chloralkali wastewater. The bacteria were grown on carriers within the bioreactor. Tests were made on the mercury removal and bacteria growth for a variety of fluctuations. The overall plant consisted of pH adjustment, bioreactor and an activated carbon filter to remove remaining traces of mercury (Figure 8). The system was carefully monitored and many parameters were predetermined (Döbler, 2000).

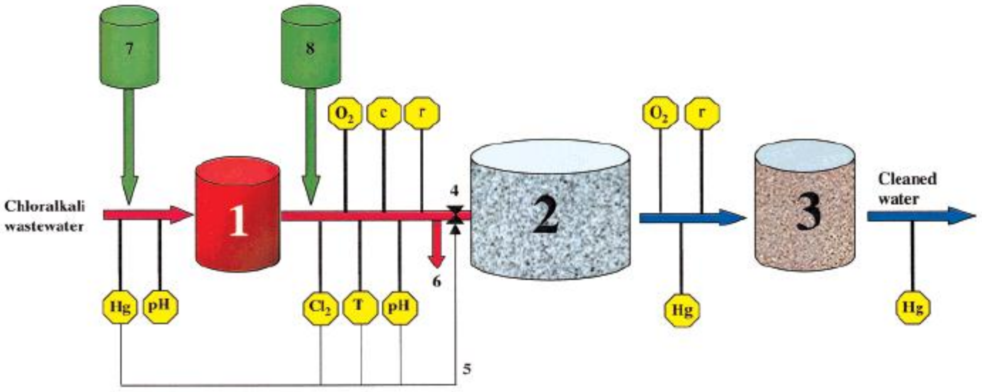


Figure 8. A schematic illustration of the pilot plant for microbial mercury remediation. Numbers refer to tanks or valves, yellow octagons to monitors (Döbler, 2000).

The retention efficiency was instantly 82 % and after 10 hours the efficiency was up to 97 % (Döbler, 2000). A 5 days operation time was studied and the overall efficiency over the bio filter was estimated to be 95 %. Even though the microorganisms could coop up to 10 mg/L of incoming mercury the respiratory activity was reduced and needed recovery of several days to grow up an enough large bacteria culture. To be able to run a continuous technical scale bioreactor operation, an automated dilution of elevated mercury concentrations are required through cleaned water from the bioreactor or by implementation of a large buffering tank rather than having the bypass function as in this pilot plant.

The elemental mercury was in this case captured as metallic mercury within the bioreactor. The reduced mercury is accumulated in form of small droplets of metallic mercury within the microbial biofilms (Döbler, 2000), from which it can be ultimately eluted and recycled back into the process.

3.5 Membrane filtration

Membrane filtration is applied for a variety of polluted water such as; drinking-, ground-, surface- and industrial water (U.S. EPA, 2007). In this technique some kind of barrier is used, often a semi- permeable membrane which separates contaminants in the water with help of pressure. The contaminants are accumulated in one stream and the water through the semi- permeable membrane is cleaner. Membrane filtration follows often a pre-treatment step e.g. precipitation/co precipitation to form larger particles that are more effectively removed by the membrane media (U.S. EPA, 2007).

There are different types of membrane filtration processes that can be applied depending on the characteristics of the pollutants in the water to be treated. There is a variety in membrane materials, operating modes and modules configurations as well as selection of the pore size of the membrane etcetera (U.S EPA, 1997). The selection of pore size is based on the molecular weight or the size of the heaviest/largest contaminant in the water and also upon the needed pressure to force the water through the filter (U.S. EPA, 2007). Membrane filtration can roughly be divided into 4 types depending on the size of contaminants to be rejected. There are micro-, ultra- and nano- filtration and there is reverse osmosis, all of them presented next.

Micro filtration (MF)

MF is used to remove suspended and colloidal particles and has a pore size somewhere in-between 0.05–10 µm. It removes molecules with a molecular weight larger than 100 000 Daltons = g/mole. The required pressure is often 100–400 kPa but can range in between 5–5000 kPa (Wang, 2011). MF is often used as a pre-treatment step before Nano filtration, reverse osmosis or other treatment technologies to remove larger particles, heavy molecules or virus (Wang, 2011).

Ultra filtration (UF)

UF has often a filter size of 0.01–0.1 µm that is used to primarily remove oils, suspended particles and biological solids (U.S. EPA, 2007) and can filter out other contaminants with a molecular in- between 300 and 500 000 g/mole according to (Wang, 2011). The required difference in pressure over the filter to move water through a UF membrane is according to (U.S. EPA, 2007) 34.5 to 689 kPa and according to (Wang, 2011) the operating pressure is in the range 200- 700 kPa.

Notable is that the effectiveness of a UF membrane is sensitive to e.g. suspended particles, colloids, organic compounds and other contaminants since these can cause membrane fouling (U.S. EPA, 2007). UF alone cannot remove free ions and smaller complexes, why precipitation often is used to form larger colloids that can be trapped by a UF membrane. There is thus a contradiction whether or not the membrane shall be loaded with particle- and colloidal rich water.

Nano filtration (NF)

NF has a pore size of below 0.01 µm, usually 0.001 µm. It is often used in softening and the removal of organic contaminants and employs the principles of reverse osmosis (Wang, 2011). It often removes contaminants heavier than 200 to 1000 g/mole but sometimes the molecular cut- off is increased up to 100 000 g/mole (Wang, 2011). The required operating pressure is often in the range 600–1000 kPa. Figure 9 summaries the 4 separation processes and what they typically rejects.

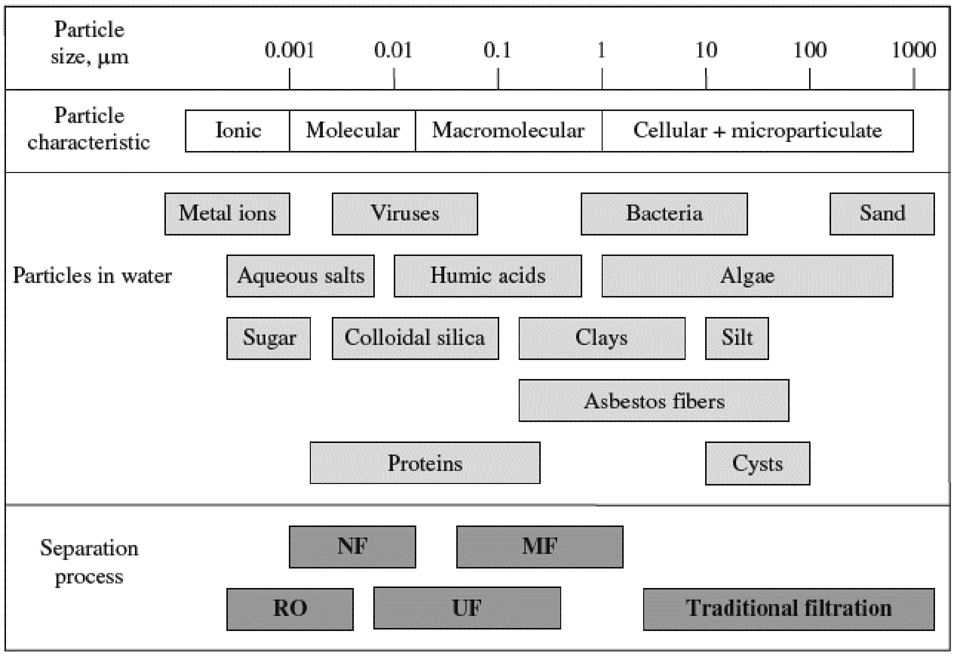


Figure 9. An illustration of different pressure-driven membrane filters (various sizes) i.e. microfiltration, ultrafiltration, nanofiltration and reverse osmosis (Wang, 2011).

Reverse osmosis (RO)

In RO a solvent with a high concentration of solutes (salts and other pollutants) is forced to a lower concentration through a semi permeable membrane by applying a pressure in excess of the osmotic pressure on the side with the high solute concentration. In this way the solvent (water) goes through the membrane leaving most of the solutes behind. The required pressure is in general 5000 – 10 000 kPa over the membrane with a pore size less than 0.002 µm (Wang, 2011).

The applied pressure must be in excess of the osmotic pressure but gets to a point where it no longer is able to be above the osmotic pressure and no more water can pass the membrane. If the applied pressure however is forced to overcome the osmotic pressure a point is reached when the membrane becomes fouled by precipitated salts and other undissolved material in the water. Reverse osmosis rejects organic solutes with molecular weight similar to fulvic- and humic acids, lignin and detergents (Wang, 2011) as well as microorganisms, particulate matter, contaminant ions and dissolved non-ions (Wang, 2011).

Nano filtration and RO which uses semi- permeable membranes differ from MF and UF (micro porous membranes) since the applied pressure over the membrane has to account for the osmotic pressure from the opposite side of the membrane. There are ways of calculating pressure gradients, flux rates and recovery of membranes for different modes i.e. deposition and suspension which in depth is described by (Wang, 2011).

Deposition mode (Dead- end filtration)

In a deposition mode, often called "dead- end filtration", the membrane acts like a simple barrier to the contaminants in the water where the incoming water hits the membrane to the normal (perpendicular). Contaminants that are stuck on the membrane will form a layer (cake) which decreases the flow rate of water that goes through the membrane which often means that the filter needs to be switched. In this mode there are thus only two streams, the feed and the filtrate. Contaminants larger than the pore size are rejected and leaved at the surface of the membrane forming a cake, see Figure 10.

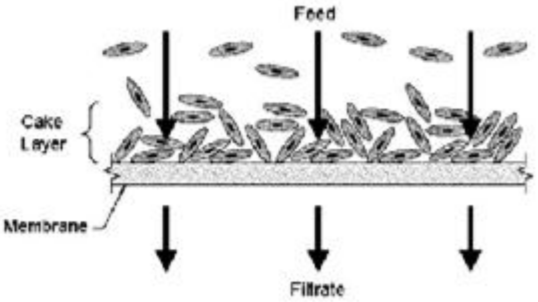


Figure 10. A schematic view of a membrane in deposition mode "dead- end filtration". (Wang, 2011).

Suspension mode

In this mode the feed is applied parallel to the membrane with the objective to minimize contaminants to accumulate on the membrane surface thus to reduce fouling and to avoid a decrease in flow through the membrane (Wang, 2011). This operation mode has three fluxes, the feed, the filtrate and a concentrated (or reject) stream as seen in Figure 11. The suspension mode can be divided into three different models i.e. cross- flow model, plug flow reactor (PFR) and the continuous stirred tank reactor (CSTR) model. The feed flows through the membrane where water is forced through the membrane material by a pressure perpendicular to the water stream direction. A concentrated stream is obtained in the end of the membrane (Wang, 2011).

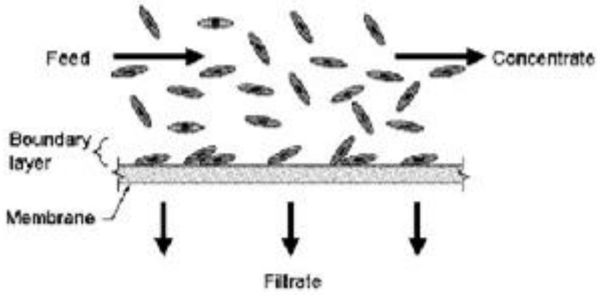


Figure 11. A schematic view of a membrane in suspension mode(Wang, 2011).

In a cross- flow system mode microfiltration is often used, mostly referred to as cross-flow microfiltration (CFMF), where the primary component in the system is a tubular fabric filtration curtain with a dynamic inner surface and is explained in detail by (Broom, 1994).

Mercury removal by membrane filtration

A pilot- and full scale study was done by Broom (1994) on combining ordinary precipitation followed by CFMF to remove heavy metals including cadmium and mercury from a mixed plating waste stream.

The plating water contained various heavy metals where the overall mercury removal was observed to be around 98.5 % (Broom, 1994). The average pressure over the CFMF modules was 150 kPa. The permeate flux decreased from 110-150 down to 50 L/m^2, h over a 24 hour period and was then cleaned by water jets and acidic solution at pH 4 to get rid of the formed filter cake.

The total cost for this full scale plant was estimated to be £120 000 as capital cost, £0.17/m^3 as O&M (including membrane replacement, labour, chemicals and washing) plus electricity which was 0.67 kWh/m^3 (no electricity cost estimated) (Owen, 1995). An economical assessment of membrane costs for various membrane materials (polymeric and ceramic) for a large set of different operating conditions such as cross-flow velocity, Trans Membrane Pressure (TMP) and daily water inflow. It turned out that the total cost (excluding land requirements) was decreased with increased water flow, higher TBP and decreased cross- flow velocity. Ceramic membranes have a longer lifetime, 10 years estimated compared to polymeric membranes, 5 years. Still the lowest total cost was obtained with polymeric membranes 20- 40 £/m^3 treated water compared to ceramic membranes, 81 £/m^3. Notable is that the pilot plant tested had a large inflow, 1000- 6000 m^3/day and did not consider heavy metal removal but only BOD, TOC, suspended particles and coliform.

4 More needed investment techniques

This chapter is for the techniques which neither discussed in theoretical chapter nor will be used in the comparison part. These are the techniques which might not be that common to use for wastewater treatment compared to the most common ones mentioned in the theoretical chapter, although good removal efficiency has been achieved by utilizing these techniques. The techniques might be applicable at Välen deposit site, that's why any further investment in future may be needed.

Mersorb

Mersorb is a mercury adsorbent material which is a sulfur-impregnated activated carbon bed (U.S EPA, 1997). It is an adsorption method using sulfur-impregnated that activated carbon is a post sulfide treatment. Sulfur is added to the wastewater, and then insoluble mercuric sulfide is produced. In fact it is a combination of precipitation and adsorption which precipitation occurs before adsorption by activated carbon. In a case study which was done by Tonini et al 2003, the chlor-alkali wastewater characteristics included pH 4–-11, chloride content 80–260 g/l and total Hg 6,000–70,000 ppb using cartridge filters with 0.5 µm filters before and after the adsorption facility. The flow rate to the system was about 0.53 l/m, the empty bed contact time about 35 minutes and the adjusted pH was 10–11. The Influent mercury concentrations were measured about 4.5-86 ppb. Before the breakthrough, the mercury concentration in effluent was determined. The median was 112 ppt with the total result in a range from 25–413 ppt. Through running the pilot plan, the average mercury efficiency was achieved of about 98.64% considering the discharge limitation (Tonini, 2003).

Xanthate Treatment

Starch xanthate is an adsorbent for removing heavy metals from wastewaters. Beside using this adsorbent, the other additional treatments such as sedimentation, filtration and activated carbon are used in order to get higher removal efficiency (U.S. EPA, 1997). According to Campanella and colleagues (1986), by applying starch xanthate treatment for different initial mercury concentrations in synthetic and chlor-alkali wastewater, very low mercury concentrations were obtained. For example a high initial concentration was reduced from 100 to 0.001 mg/l following 0.45 µm filtration. All final mercury concentrations are very low compared to their initial concentrations (U.S. EPA, 1997).

Adsorption by clay minerals

To increase the sorption capacities for natural materials, surface modification is an attractive method which has been tested on many various materials. Mostly acids and bases have been used as modifiers.

A promising but relatively new direction is the use of naturally occurring clay minerals that after being surface modified has shown good adsorption capacities for heavy metals. These methods include modifications with acids and bases, replacement of natural exchangeable cations with organic cations, and impregnation of organic molecules etcetera (Krishnan, 2003). The mercury adsorption on natural clay (90 % Kaolinite mineral) impregnated with either 2-mercapto benzimidazole ($C_7H_6N_2S$) or humic acid was investigated. It was shown that MBI- clay and HA-clay were 6.3 and 4.2 times more effective than the unmodified clay. The MBI- clay showed the overall best results with a 100 % mercury removal under a pH of 4- 8 with an initial concentration of 50 mg Hg^{2+}/L.

The disadvantage of using these clays is the long contact time required, which means that a relatively low flow or a large volume is needed. The removal efficiency was proven to increase with lower initial concentration but the tested concentration was the 17.5 mg/L which is way more than at the leachate water at Välen. Also, the efficiency decreases with lower temperatures, with the lowest tested at 30 °C, and the leachate temperature at Välen has been in the range 6–13 °C. However, this test was a batch experiment where mercury and the adsorbent were added in a solution tank batch wise and it is unknown how to operate a continuous mode with the clay in e.g. columns.

Other adsorption process

There are other adsorption processes which are compared to each other, in terms of mercury removal efficiency, based on Freundlich adsorption equation. The Freundlich adsorption equation is:

$$log\frac{x}{m} = logk + \frac{1}{n}logc_e \qquad [2]$$

x= the amount of mercury adsorbed

m= the amount of adsorbent

k and $\frac{1}{n}$ = Freundlich parameters

c_e= equilibrium concentration

k represents the sorption capacity and $\frac{1}{n}$ represents the sorption intensity (U.S. EPA, 1997).

These adsorption processes include **BPHC** (bicarbonate-treated peanut hull carbon), **MHBB** (modified Hardwickia Binata bark) and **Coal Fly Ash** (U.S. EPA, 1997). According to Namasivayam and Periasamy (1993), based on a bench-scale study using initial mercury concentration from 10 to 20 mg/l, the BPHC effectiveness in mercury (II) removal -due to having higher porosity and moderate ion exchange capacity- is seven times higher than GAC. In addition regarding different reports, the mercury desorption ratio from BPHC using 0.6 M HCl was 47% while for GAC it was 13% (U.S. EPA, 1997). In another experiment, the desorption ratio of mercury from BPHC and GAC using 1.0% KI (potassium iodide) were 87% and 24%, respectively (U.S. EPA, 1997). There is no full scale data for this adsorbent.

In other research by Deshkar et al., 1990, the role of modified Hardwickia Binata bark (MHBB) in adsorption of mercury (II) was studied. They showed that the higher pH the higher sorption of Hg (II) and the ideal contact time was 2 hours. The best function of MHBB is when the concentration of mercury is below 20 mg/l (Deshkar, 1990).The adsorbent material was effective in mercury (II) removal from water but it was not as effective as GAC (U.S. EPA, 1997). Coal fly ash is an industrial waste solid used as an adsorbent in mercury removal processes (Sen, 1987). The best performance of this adsorbent was seen in pH ranging 3.5-4.5 (Sen, 1987). Although it has a good adsorption capacity for mercury (II) (Sen, 1987), but according to the Freundlich parameters, the coal fly ash efficiency in mercury removal is not that high compared to BPHC.

SAMMS (nano technology adsorption)

SAMMS “Self-Assembled Monolayers on Mesoporous Supports” from Stewards Advanced Materials Incorporation is a family of adsorbents that uses silane chemistry. Silanes have the advantage to merge both carbon chemistry and silicon chemistry to design very unique chemicals (Steward Advanced Materials Incorporation, 2011). The SAMMS adsorbents are made of a silane which has two active ends. In one end there is a hydroxyl that is adsorbed on the surface of an adsorbent support. On the other end is located the active adsorbent. For mercury adsorption a sulfhydryl (-SH) is chosen as the adsorbent molecule (Steward Advanced Materials Incorporation, 2011) and (EPA, 2007).

The reason why SAMMS are good adsorbents depends also on their large specific surface area of 500–1000 m^2/g of sorbent. The sorbent material (sorbent support site) is often made of silica (SiO_2) that has been engineered to have a large quantity of mesopores, which is what the other part of SAMMS refers to. With a large specific area, more silane containing thiols can be attached. Figure 12 shows an illustration of this. The middle picture is one pore with its whole surface covered by silane attached through self- assemble, the yellow is thiols. Mercury (blue) is then adsorbed by the thiols. The mesopores must not be too small, but have to be able to let the mercury to diffuse into them (Steward Advanced Materials Incorporation, 2011).

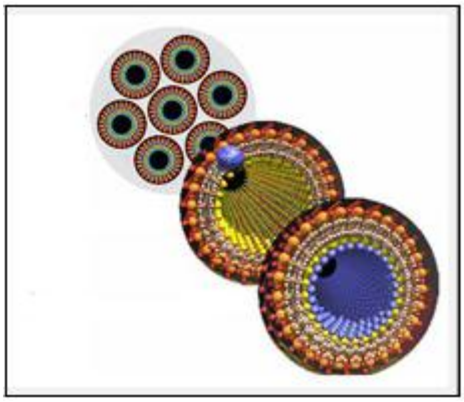


Figure 12. This Figure illustrates a SAMMS sorbent (in this case a zeolite) with mesopores. (Incorporation, 2011).

SAMMS has extremely fast kinetics and mercury has through tests been reduced to below 1 ppt. The recommended pH for optimal reduction is 4 to 8 but good results are obtained from a pH of ~3 to 12 (Steward Advanced Materials Incorporation, 2011). The typical capacity is 0.4–0.6 grams Hg/gram of a Thiol-SAMMS for mercury concentration of 100–200 ppm (Steward Advanced Materials Incorporation, 2011). Most cations and anions have a minimal impact on the performance and since it is chemically specific and hydrophobic it enhance its ability to remove mercury in the presence of organics in aqueous waste streams (Steward Advanced Materials Incorporation, 2011).

SAMMS were used in the study by Klasson (1998 b) and were studied along with Keyle:X and SIR-200 in the long term run for mercury removal. This technique seems to be commercial but are most likely not very available at the Swedish market yet and is for this reason not further investigated in the site specific part for the case study of Välen deposit site and neither in the comparison part.

5 Välen pilot test and flow determination

5.1 Determination of leachate flow

The estimated infiltration i.e. the formed leachate water at Välen landfill is 12500 m^3/ year (Melica, 2010b). There is an uncertainty about how much that actually infiltrates and also how much of the infiltrated water that reaches the sludge well. If it turns out that almost all leachate water is drained and collected in the sludge well, then only this water is of concern and needs to be treated. However, if the flow to the sludge well is relatively low compared to the estimated value, this means that there is a large diffuse flow out from the deposit which unfortunately is hard to locate and collect. A too small flow might be unreasonable to be treated by a technique and also it might be considered not justifiable to treat a very small portion of the total leachate when the majority leaves the site untreated.

The leachate to the sludge well is measured by measuring the increased water level in the sludge well between the site visits. The increased volume is then divided by the time between the measurements. While doing the flow measurement at site, a pilot plant is designed and operated. The treatment technique chosen for the leachate is based on adsorption. The reason is that adsorption is a well proven technique for treatment of contaminated water, and sorption on activated charcoal is a technique proven for sorption of both metals (mercury in inorganic form) and organic contaminants (methyl mercury). The reason is to test this method's efficiency and applicability for the conditions at Välen.

5.2 Pilot test

The adsorption media to be selected is supposed to be appropriate to adsorb toxic metals and especially mercury in both organic and inorganic form. The adsorbent media is supposed to be sustainable i.e. removal effective, cost effective as well as to be available not too far away to avoid long transportations. Once the adsorbent media is chosen a proper contact time with the filter bed is needed to be determined. The contact time together with a given column volume will determine the flow that will pass through the columns during the experiment. Two columns are going to be placed in series to increase the chances that the effluent concentrations not exceed the guideline values. Further, this enables to conduct and assess the breakthrough curve of total mercury.

GAC and columns design

To evaluate the effectiveness of the filter and to plot the breakthrough curve, measurements of incoming and effluent water will be done. The measurements will be taken frequently within a run time of approximately one month. This time might be short in order to ensure the actual breakthrough time but is within the time frame for the master's thesis. The ambition is to have enough time to plot the breakthrough curve for the first column and get the first part of the second curve (second column) to see when the effluent concentration exceeds the guideline value for mercury. Good results will give the basis for calculations of the real breakthrough time and an understanding of how many columns and their dimensions that are required to treat the leachate water by this technique for the real conditions.

The adsorbent media selected is a coal based GAC (Granular Activated Carbon). It is direct activated i.e. it has only been carbonized and activated and has a mesh size of 12x40 (0.425–1.70 mm). GAC is good for long term column water treatment because it can be backwashed and also thermally regenerated to get rid of the adsorbed contaminants for the purpose to reuse the adsorbent media. The lossess during regeneration for this GAC is approximately 10–15 % (Legros).

The size of each column is 1 m in height and as it should be filled with gravel and sand to get appropriate hydraulic flow, it is assumed that it should be filled with approximately 30 cm of gravel/sand and 50 cm of GAC. This is in order to have space for a water table above the GAC and to avoid water to be spilt during transportations and to decrease the risk for overflow during the experiment. All these assumptions are made in order to be on a safe side. The 50 cm bed height equals to a bed volume of 22.6 L per column.

The recommended contact time for this GAC is in the range 10–60 minutes (Moden, 2011), and since the concentrations of not least mercury is low compared to performed experiments in laboratories, a contact time of totally 60 minutes has been determined (30 minutes per column bed). This contact time gives together with the bulk volume the necessary flow (Q) through the columns and is given by formula [1]:

$$EBCT = \frac{V}{Q} \rightarrow Q = \frac{V}{EBCT} \rightarrow \frac{22.6L}{30\text{min}} = 0.75L/\text{min} \qquad [1]$$

Where V is the bulk volume of GAC in contactor, (L), Q is the volumetric flow rate (L/min) and EBCT is the contact time in (min).

Hence, the required flow is calculated to be 0.75 litre per minute.

The initial parameters and their values for the pilot experiment are presented in Table 7.

Table 7. Initial pilot plant data.

Parameter	**Unit**	**Value**	
Carbon type		*AquaCarb 208 EA* , 12x40 mesh (Direct activated coal based GAC)	
Column Inside Diameter	m	0,24	
Column Area	m^2	0,045	
Bulk Bed Volume	L	22,6	
Apparent Bed Volume	L	20,35	
Bulk Bed depth	m	0,5	
Apparent Bed depth	m	0,45	
Bulk Density of GAC	kg/L	0,42	
Apparent Density of GAC	kg/L	0,467	
Flow rate	L/min	0,75	
Hydrolic loading	L/min*m2	16,6	
EBCT (each column)	min	30	
Hg (unfiltered) EQS	µg/L	<0,07	(Gothenburg guideline at point of discharge)
Weight of GAC (per column)	kg	9,5	
Run time	days	30	

<u>Parameters that can be determined after the experiment (if breakthrough is reached) are:</u>

- The real flow rate (through flow measurements)
- Empty bed contact time and number of columns.
- Column nominal diameter and mass of GAC/column.
- Bed depth.
- Real contact time needed
- Real breakthrough time (change out period)
- Volume of water treated per change out period.

Column preparation

Sand in various sizes is filled in the columns in order to hold a good hydraulic flow. Three different sizes of sand were used: 1.2–2 mm, 3–5 mm and 5–10 mm, see Figure 13. The largest fraction (5–10 mm) was further sieved into two sizes; 5–8 mm and 8–10 mm and hence totally four layers were used. The distribution was to start with the largest fraction in the bottom of the column and then in decreasing size upward the column. A totally height of approximately 30 centimetres was supposed to be filled.

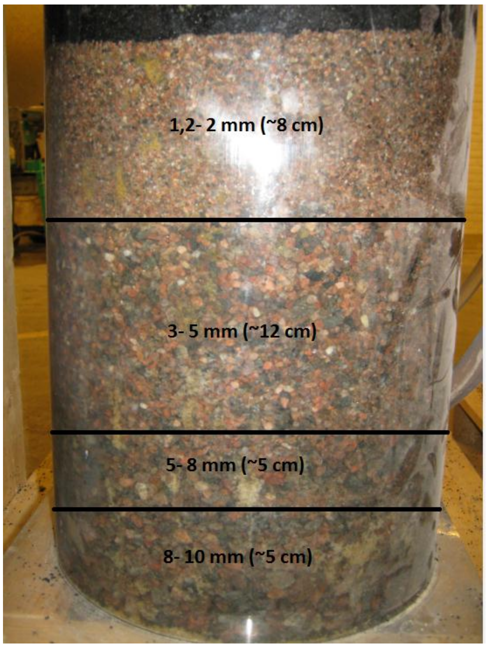


Figure 13. The distribution of sand in the columns. The size of sand is decreasing with height to give a good hydraulic flow. The layer thickness and sand sizes is seen.

A GAC bulk bed height of 50 centimetres had been predetermined to be a good height for giving space for the sand and a water table as previously mentioned. The density given from the manufacturer of 420 kg/m^3 should be valid for a backwashed and drained condition. To be sure that the density actually is valid for a wet condition, as during operation, the GAC was initially weighted and the bed height measured. A height of 51 centimetres with the given density corresponds to a weight of 9.3 kg.

The procedure for filling the columns with GAC was similar to for filling the sand. Initially a shallow water table was present above the sand. GAC was then filled to reach the top of the water table. Then more water is added and GAC is again filled to the top of the water level until all GAC is filled. In this way it can be avoided to get a large amount of GAC slurry compared to if filling the column with all GAC at ones and then pure water afterwards.

Figure 14. The columns configuration.

The final columns had a 30 cm layer of sand with a 49 cm of GAC layer above. Before going out to the site the whole column system is connected containing water without any air. During transportation to the site the columns were covered and the tubes secured in order to keep the water within the system.

Pilot plant design

A pump was placed in the sludge well to pump the incoming water from the drainage pipe to a 1 m^3 tank placed upon the roof of a container. A flow of 0.75 L/min will leave the tank to the first column, see Figure 15. The water level is kept constant in the column by letting the outgoing tube have the same level. The first column was placed 20 cm higher than the second column, in order to avoid using a pump between the columns. Pipes were attached to avoid the columns to be overflown as well as the outgoing tube from the 2nd column; see Figure 16.

Figure 15. The pipe connected between the pump and the tank as well as the tube from the tank to the columns through an opening in the container (left). A close look in the sludge well and the pump can be seen (right).

Figure 16. To the left is seen the second column with its incoming water pipe and the safety pipe. To the right is seen the tubes attached to the safety pipe that leads to a bucket where also the outgoing tube is attached in the bottom. This tube goes straight out from the container to the ditch/creek.

The initial water volume in the sludge well was 2.5 m^3 that could be pumped to the tank. Before taking samples, water was flown through the system over 2 hours to let the initial clean water in the system go through and be totally replaced by the leachate water.

The total number of bed volumes of water within a given time is calculated as follows:

Bed volumes per minute is equal to 1/EBCT = Q/V. Where V= the volume of 1 GAC bed (22.6 L). BV/minute is then multiplied by the time that water has been let to the columns (minutes) which gives the number of BV (bed volumes) that has passed one column. This is then multiplied by 2 to get the total number of BV considering both columns together.

Table 8. Pilot plant measurement data. Flows to the sludge well, flow to columns and calculated bed volumes through the columns are shown.

Date	Flow through columns (L/min)	Bed volumes through columns (total)	Average flow to L1 (L/min)	Direct flow to L1 (L/min)
11 May	0.75	9	-	-
12 May	0.75	31	-	0.15
13 May	0.5	31	-	0.15
14 May	0.4	49	-	0.075
15 May	0.4	57.5	0.066	0.045
16 May	0.3	41	0 08	0.055
19 May	0.3	35	0 06	0 22
20 May	≈0.1	6	0.086	0.135
21 May	0	0	0.079	0.018
23 May	0	0	0.074	0.035
24 May	≈0.06	5	0.074	0.1
26 May	0 5	4	0.076	0.09
29 May	0 5	17	0.088	0.035
4 June	0.05	2	0.08	0.13
7 June	0.05	4	0.1	-
9 June	0.05	2.3	0.065	-
10 June	0.5	4.5	-	-
15 June	0.75	6.5	0.04	-
			0.074= 0.1 m^3/d	0.095

A problem with clogging was identified in 19th of May because the water level in the first column was rising, and some amount of water went directly out through the safety pipe. Both columns were hence receiving less flow than what was regulated from the tank to the first column. Yellow coloured foam was also observed on the surface in the second column which indicated that it received some clogging material from the first column.

Both columns were backwashed with tap water separately in an attempt to get rid of clogging material in the GAC at 24th of May. A sand filter was also installed prior to the first column to act as a pre-treatment step to filter large organic matters, particles and sludge that leaves the tank. Three sizes of sand, the same as used in the columns except the largest size, were filled in a steel tank to about 20 centimetre height which enabled to have a larger constant flow to the first column. The flow from the tank to the sand filter is regulated to 0.75 L/ min and the water from the sand filter is held at 0.5 L/min. The difference in flow over the sand filter gives a constant water level in the sand which enables a constant flow of 0.5 L/min to the first column. In case of a clogged sand filter the sand can be more easily backwashed than the columns. See Figure 17 for the construction.

Figure 17. The sand filter and the tube from the tank are shown (left). On the end of the tube is a throttle valve. There is three tubes attached on the steel tank (right), one goes to the first column, one is for stabilizing the water level in the sand filter an and the third is for over flown water that goes to the bucket inside the container.

The problem with clogging was again suspected. Another backwashing was done on the 9th of June for the columns and the sand filter as well as adding an extra layer of finer sand in the sand filter since it was believed that the clogging material is going through the sand and clogs the first column.

5.2.1 Sampling scheme

Samples will be taken on the incoming water, after the first and second column for calculation of the removal efficiency, and in order to plot a breakthrough curve for the columns. Samples will be taken every third day during 30 days, hence 10 sampling occasions.

Measured parameters and their analysis method can be seen in Appendix 2. The metal analyses were done by an external laboratory (ALS Laboratory group).

The sampling procedure was done as shown in Table 9. Samples for metal analysis and methyl mercury was taken every 10th day together with samples for Chalmers analyses and field measurements. The sampling frequency for unfiltered total mercury is every third day so a breakthrough curve will be drawn only for unfiltered total mercury. The reason for having only 3 measurement occasions for the rest of the metals and methyl mercury is a matter of cost.

The parameters that were measured in field were temperature, oxygen, conductivity and pH. The parameters measured additionally at Chalmers are None Purgeable Organic Carbon (NPOC), Dissolved NPOC, Total Nitrogen, Dissolved Nitrogen, chloride and total solids. NPOC is the total organic carbon except volatile carbon.

When running unfiltered samples NPOC and TOT N are analysed, and after pre-filtration, dissolved NPOC and dissolved N are held. The filtration was made by using a glass fibre filter with a pore size of 0.7 µm. Dissolved NPOC is thereby the fraction smaller than 0.7 µm and is more likely to be found free in the water.

Table 9. The sampling scheme. The total numbers of samples are shown.

Sampling occasions	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**Tot**
	11/5	**14/5**	**16/5**	**20/5**	**23/5**	**26/5**	**29/5**	**4/6**	**7/6**	**10/6**	**samples**
V3a (unfiltered) + P	3					4				4	11
V3a (filtered)	3					4				4	11
Field measurements	3					4				4	11
Chalmers laboratory	3					4				4	11
Methyl mercury	3					4				4	11
Unfiltered total mercury only		3	3	3	3		4	4	4		24

6 Pilot plant results

6.1 The leachate flow

The leachate flow that has been measured during one month (11 May –15 June) was in average 0.074 L/min which equals 0.1 m^3/day. This amount which is the incoming water to the sludge well is just 0.3 % of the estimated infiltration into the deposit area (5 ha) of 34.2 m^3/day as a yearly average. The meteorological conditions were before the measurements relatively dry compared to resent years. During the latter half of the measurement period, there has been some rain, but any significant change in the inflow to the sludge well has not been observed. This time of the year is also relatively dry compared to the autumn, which means that this short time period at this time of the year cannot represent a proper estimation of the yearly average flow. However it gives an approximate idea of how large share of the infiltrated water that is drained to the sludge well.

6.2 Sorption efficiency of Hg

The effluent concentration of unfiltered mercury after the first and second column shows 66 % and 21 % mercury removal respectively with a total percent mercury removal of about 74% over the whole system. For methyl-mercury these values are 78% and 34% for the first and second column respectively. The effluent concentrations did however not meet the guideline value limitations. The average effluent total mercury concentration was 65 µg/l compared to the guideline value of 0.07 µg/l. For methyl-mercury the guideline value is 10 ng/l while the achieved average effluent concentration was 25 ng/l. Neither total mercury nor methyl-mercury was under their guideline values at any time during the pilot test.

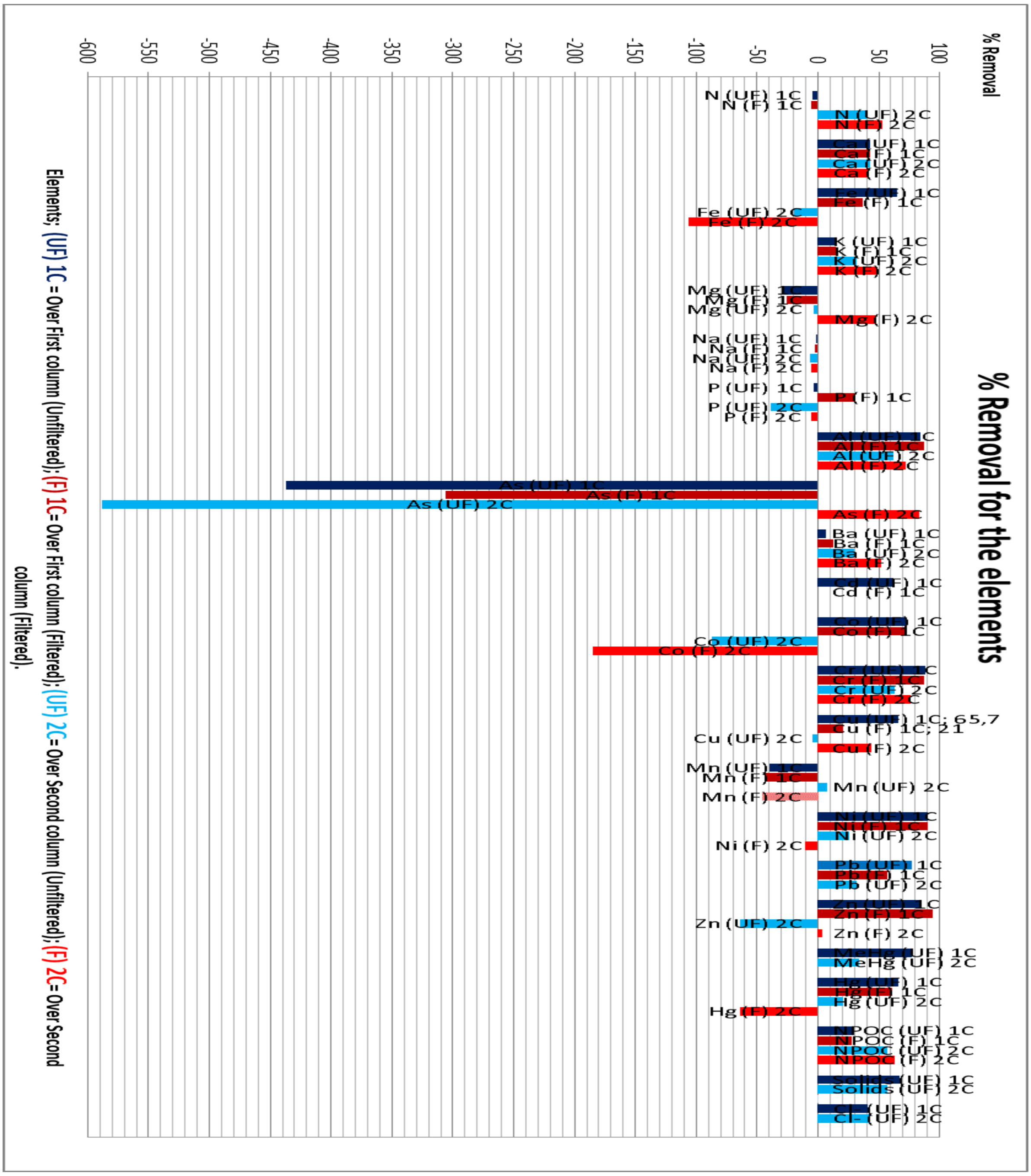


Figure 18. The average percent removal performance by the GAC columns for each element analyzed in the pilot study. The percent removal over both columns is seen as well as for unfiltered and filtered i.e. for species/complexes above or under the size 0.45 µm 0.7 µm in case of N and NPOC).

6.3 Sorption efficiency of other elements

As can be seen in Figure 18, the GAC manage to remove total solids and NPOC fairly well. Dissolved NPOC (filtered) showed the same concentrations as total NPOC which indicate that almost all organic carbon species are smaller than 0.7 µm in size. Both columns effectively adsorbed both NPOC and dissolved NPOC (below 0.7 µm). For total solids, the size distribution is unknown. The total solids include both suspended and dissolved solids. Metals like Ca, Al, Cr, Pb, Ni, Cu, Zn, Cl^- and Hg are removed quite well while Mg, P, Na, Co, Mn and not least As are not effectively adsorbed and rather increased in concentration. A substance can be removed effectively in either of the two columns or in both but it is the total removal efficiency over the whole system that matters. In case of Arsenic, the net concentration increases over both columns. The GAC seems to release As, Mn and Na since these metals' concentrations increases net over the system, see Appendix 5.

It is hard to see whether the GAC is especially good for adsorbing the unfiltered or the filtered species better over the other. It differs between the substances. It would be interesting to see if the GAC removed free cations better than larger complexes or vice versa, but this is not possible to judge as the 0.45 µm filter does not filter out just the cations which are much smaller.

It seems that for elements as Fe, Ni, Pb and Hg the removal efficiency for unfiltered samples is better compared to their filtered (dissolved metals) ones. It might be reasonable to say that these elements contain smaller complexes than the rest of the elements. The removal efficiency for most other elements shows a better removal for filtered samples. It makes sense to say that dissolved metals have been adsorbed to the filter more than undissolved metals.

The sudden increase in As concentration is seen after the first and second column for the first sampling date. It is not reasonable to consider the variation of As concentrations as average values since the only strange values are seen just for the first sampling date. Unfortunately there is no pH and oxygen measurement for that date (11 may), hence it is hard to correlate those strange values to the mentioned parameters. The other errors during sampling or by lab can be the other reasons for such strange values. It is not reasonable to assume that GAC contains As. These strange values are seen for Mn as well. In this case the first sampling date shows a normal behavior, but the strange values are seen in the second and thirds sampling dates since the concentrations have been increased over the columns.

There are three unfiltered results but only two filtered, which might influence the results. Also some data are unreliable as the filtered results are higher at some occasions relative the unfiltered.

The data in Figure 18 and Appendix 5 are the calculated mean values of the samples, 3 dates for all substances except total unfiltered Hg which has 10 samples. The percent removal efficiency varies from date to date. Figure 19 shows the removal efficiency for (unfiltered) total Hg during the whole experiment. Surprisingly the removal efficiency is not high initially which often is the case in similar removal graphs

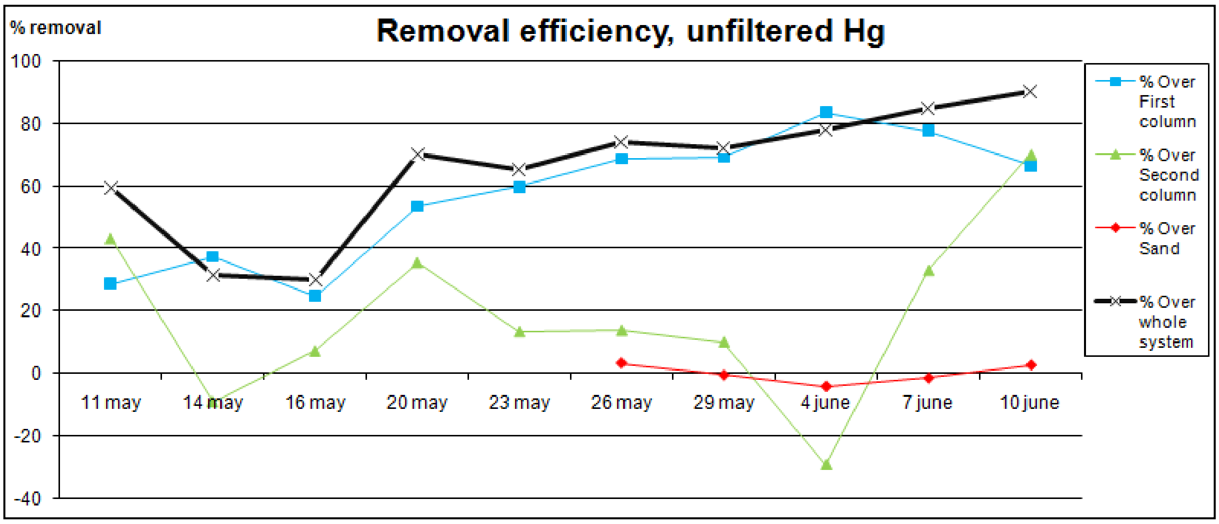


Figure 19. The removal efficiency for total unfiltered Hg for all 10 occasions. The colored (blue, green and red) graphs illustrates over first column, second column and the sand filter respectively. The black line is the total removal efficiency over the whole system.

The removal efficiency has an upward trend with an exception for a dip at 14 and 16 of May. It starts with a 60 % removal and ends with a 90 % removal after 150 bed volumes (BV). The sand filter did not remove any mercury. The sand filter neither removed any solids which some Hg is bond onto. That is also why the first column easily gets clogged, it adsorbs solids that just passes through the sand filter and even has been increased (- 32 % removal over sand). The removal efficiency is often reduced after the material gets saturated. After this few BV through the column system this cannot be noticed. The two dips in removal efficiency for the second column are harder to explain. The 14th of May is only one occasion after the start of the experiment. The negative removal indicates that no Hg has been adsorbed, which probably has to do with that other species was more easily adsorbed in the initial phase.

As solution pH increases, the amount of hydroxide ions (OH^-) increase and then the surface charge of activated carbon decrease. The positively charged metals ions are adsorbed to the activated carbon surfaces in this way (Paul Chen and Lin, 2001). It would be good if pH had been measured on 14th of May and 4th of June and then it was possible to assume that a sudden decrease in pH might be the reason for having higher concentration of Hg due to repulsion between positive charges. A slight decrease in Hg removal is also seen over the sand filter at 4th of June. The weird matter is that on 14th of May and 4th of June, the removal efficiency over the first column has been increased.

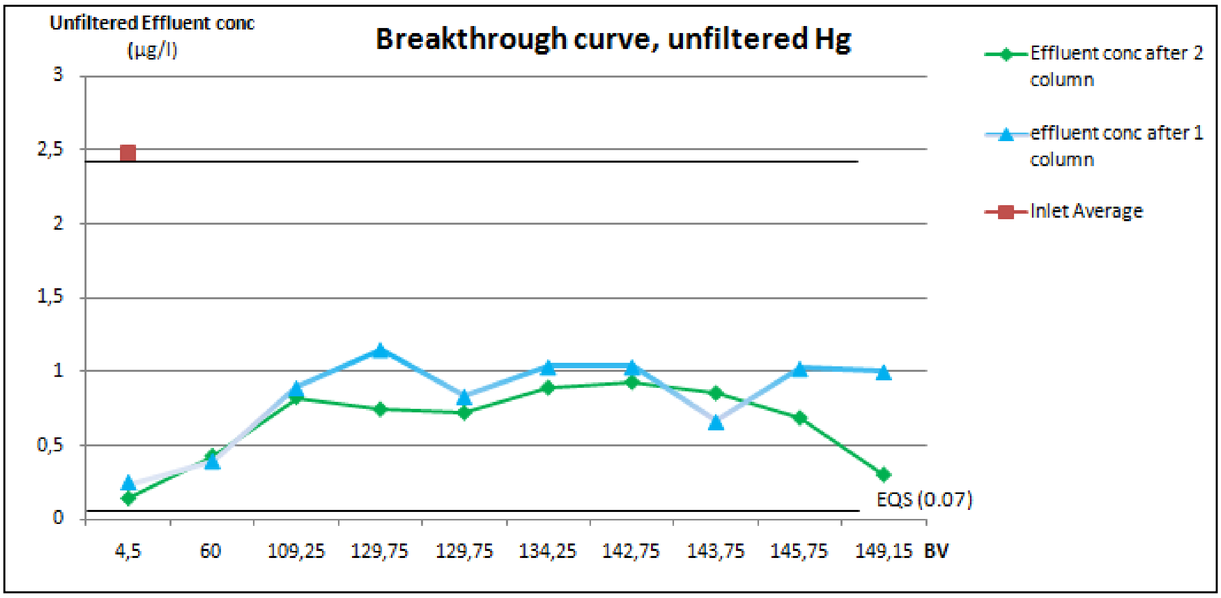


Figure 20. The breakthrough curve for unfiltered Hg showing the number bed volumes passed through the columns.

The total unfiltered (dissolved) Hg (Figure 20) do not reach breakthrough during the time of the field experiment. The amount of bed volumes (BV) was much less than expected prior to the field experiment. Due to lack of water in the sludge well and the disability to maintain a constant flow of 0.75 L/min as predetermined, fewer BV went through the columns, and is probably the reason why breakthrough never was reached, see Figure 21. Nevertheless, the effluent concentration is always above the EQS even from start. The removal efficiency was surprisingly low from the start of the experiment. The effluent concentration follows the changes in the influent concentration which is why the effluent concentration in the diagram does not increase towards breakthrough. If the influent concentration is constant the effluent concentration increases with the GAC being more saturated. The removal efficiency is good for Hg but as the concentration is very high compared to the fairly low guideline value it is not enough. Some filtered values are above the corresponding unfiltered ones, which cannot be the case. This could be due to that the filtered concentration is very close to the unfiltered sample and that the analysis devise has a measurement error.

Breakthrough was not reached and any further calculations about the change out period, maximum amount of water that can be treated and the proper column dimensions could not be done as planned.

6.4 Comparisons with guideline values

Table 10. The average of inlet and effluent concentration of all elements compared to their guideline values.

Substance	**Unit**	**Average Inlet Unfiltered (Filtered)**	**Average Effluent Unfiltered (Filtered)**	**EQS**[1]
TOC (NPOC)	mg/l	1845 (1753)	418 (342)	4
TOT N	mg/l	619 (598)	303 (228)	0.3
Cl$^-$	mg/l	98	30	100
Ca	mg/l	420 (386)	137 (133)	100
Fe	mg/l	5.6 (2)	2 (3)	0.5
K	mg/l	53 (53)	31 (24)	12
Mg	mg/l	5 (5)	8 (4)	
Na	mg/l	19 (19)	21 (21)	100
TOT P	µg/l	370 (144)	813 (101)	12.5
Al	µg/l	530 (485)	25 (13)	500
As	µg/l	8.5 (9)	301 (7)	0,4
Ba	µg/l	310 (321)	218 (136)	
Cd	µg/l	0.06 (0.06)	0.05 (0.05)	10
Co	µg/l	14 (13)	8 (11)	
Cr	µg/l	22 (18)	0.8 (0.5)	0.3
Cu	µg/l	13 (1.4)	45 (4)	0.5
Mn	µg/l	563 (525)	794 (1158)	300
Ni	µg/l	340 (573)	43 (60)	0.7
Pb	µg/l	14 (0.45)	0,36 (0.2)	0.2
Zn	µg/l	40 (27)	14 (2.5)	5
MeHg	µg/l	0.17	0.025	0.01
TOT Hg	µg/l	2.5 (0.16)	0.65 (0.047)	0.07 (0.05)

1. EQS= Environmental Quality standard.

The effluent concentrations (after the second column) were compared to the effluent guideline values for the various substances as seen in Table 10. The elements that were removed to under the guideline values were Na, Al, Cd, Zn (filtered) and Hg (filtered). Na increased in concentration over the column system but is still below the limit. Aluminium was around the limit before treatment but was efficiently removed to far below the limit. Cadmium was below the guideline value at the inlet and near the detection limit which the concentration went under. Determination of the actual removal efficiency is thereby impossible because the true concentration is below the detection limit (0.05 µg/l). For Zn the initial concentration was far above the guideline value, but was efficiently removed and below the limit in case for dissolved Zn. In case of elements such as Cr, Pb and MeHg, the removal efficiency is good but the effluent concentration is roughly above the guideline value, particularly for Pb and MeHg.

7 Site specific applicability of techniques

In this chapter the site specific conditions at Välen will be taken into account to assess the applicability of treatment techniques presented in the theoretical part. Suggestions will be made based on the studied techniques that will be the most preferable to run at Välen, site specific data have to be taken into account. The theoretical chapter gives an introduction to the methods besides the results of implementing of each technique in different case studies. The criteria mentioned in the methodology part are the main, and will here be assessed in respect to the situation at Välen. Information from the theoretical part is used to be scaled up to fit the actual conditions such as leachate flow, concentrations of pollutants and other substances, pH and the area around the deposit. The flow rate and metal concentrations are two crucial factors at Välen for scaling up the parameters. Both factors in most of the cases are much lower compared to previous studies.

The theoretical part contains information gathered mostly from other studies, with other conditions from that of Välen, which makes it relevant to see whether the techniques would be applicable also at this site and how the parameters at Välen will affect this information. It is the outcome of this chapter that will be used in the comparison part.

The real leachate flow is too low ($0.1 m^3/d$), in order to make a reasonable estimation, it is assumed that the future technique should be suggested based on $5\ m^3/d$. It is the reasonable expected flow rate that might be achievable by doing site investigation and hydrological studies in order to get more leachate to the sludge well.

7.1 Adsorption

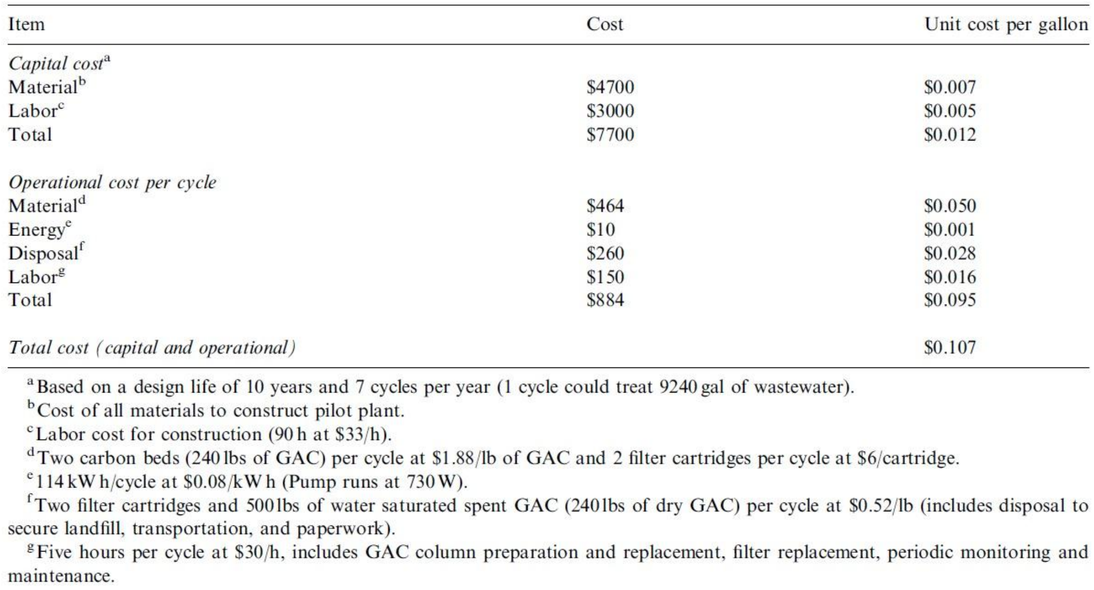
GAC

Regarding the pilot plant study at Välen, the results gained are considered as the actual results of running a technique. The breakthrough curve was not achieved, and then it was not possible to calculate the volume of treated water to reach breakthrough point. More details about the pilot plant result were discussed in chapter 6.

As mentioned in the theoretical part, the optimum pH for applying GAC ranging 4 –5 whiles the average pH of inlet at site is 8.7. The pH adjustment might be needed before and after treatment to be on the safe side. There is no available information about the cost of pH adjustment, but the cost of hydrochloric acid, sulfuric acid and calcium oxide is almost SEK13/kg, SEK1160/metric ton and SEK650/metric ton, respectively but transportation to Sweden has not been included, (Alibaba group, 2011).

Since there is not too much details in case of the cost of labours, disposal and energy, the authors thought that it would be better to use the scaled down data based on the former study mentioned in the theoretical part. The GAC treatment system includes two columns each of 30 min EBCT and 54.4 kg (120lbs) of GAC with a 100 µm pre-filter and 1 µm post-filter (Cyr et al., 2002). The cost is calculated based on the Table 11. All cost estimations were calculated based on costs in 2001 U.S dollars.

Table 11. Capital and operation cost for the GAC adsorption system (Cyr et al., 2002).



Item	Cost	Unit cost per gallon
Capital cost[a]		
Material[b]	$4700	$0.007
Labor[c]	$3000	$0.005
Total	$7700	$0.012
Operational cost per cycle		
Material[d]	$464	$0.050
Energy[e]	$10	$0.001
Disposal[f]	$260	$0.028
Labor[g]	$150	$0.016
Total	$884	$0.095
Total cost (capital and operational)		$0.107

[a] Based on a design life of 10 years and 7 cycles per year (1 cycle could treat 9240 gal of wastewater).

[b] Cost of all materials to construct pilot plant.

[c] Labor cost for construction (90 h at $33/h).

[d] Two carbon beds (240 lbs of GAC) per cycle at $1.88/lb of GAC and 2 filter cartridges per cycle at $6/cartridge.

[e] 114 kW h/cycle at $0.08/kW h (Pump runs at 730 W).

[f] Two filter cartridges and 500 lbs of water saturated spent GAC (240 lbs of dry GAC) per cycle at $0.52/lb (includes disposal to secure landfill, transportation, and paperwork).

[g] Five hours per cycle at $30/h, includes GAC column preparation and replacement, filter replacement, periodic monitoring and maintenance.

The capital cost has been calculated for a design life of 10 years and 7 cycles of operation per year. Each cycle represents the time it takes to switch the adsorbent material which means that after 154 h, 35,000 L have been treated (Cyr et al., 2002). This estimated hour has been calculated based on breakthrough curve for 3800 µg/l of mercury as initial concentration while it is 2.4µg/l for Välen deposit site. The flow rate of wastewater to the GAC system in both cases is somehow equal and it is 1 gallon/min (≈ 3.8 l/min). Hence due to much lower initial concentration, in order to make a reasonable estimation for the Välen case it is assumed that the adsorbent material could be switched every 3 months (after 2160 hours of operation) which means 4 cycles per year. In this way ~ 490,000 L of wastewater is expected to be treated by this system before replacement of new materials. Obviously the proper way of this estimation is done by drawing breakthrough curve, but as mentioned in chapter 6, the breakthrough curve was not obtained, so the only way of estimations is doing the calculations based on the assumptions.

In case of capital cost, since the flow rate to the system is somehow the same for both cases, then the amount of material used, dimensions of facility and labour all are assumed to be equal for both cases, then the same value was considered for the Välen case. The capital cost was estimated as 50,000 SEK. The operational cost per cycle was estimated as 5,660 SEK which in turn it would be 22,640 SEK for 1 year. The initial concentration is much lower for Välen, the amount of treated water would be higher and then the unit cost per gallon would be different. So the only difference between two cases is seen in the time of switching filters. Different items of capital and operational cost are seen in Table 11. The 99.8% of mercury removal was estimated as efficiency of this system (Cyr et al., 2002).

In terms of social aspects, authors believe that the technique does not create smell or noise during operation as it was run for a month at site, and even if the leachate water is smelly. It is a technique that is easy to install and its functionality is not that complicated. By using automatic devices such as pumps for pumping water from sludge well and for backwashing the columns in terms of clogging, the needs of active operation will be reduced. The GAC used in this case study is a coal based one, and it is cheap and available. Using coal may cause the natural resource scarcity while using agricultural or natural based activated carbon may be considered as a more eco-friendly option. Chemical or thermal methods are two options for regeneration of spent activated carbon which mercury-rich solution or mercury-enriched vapour is produced at the end (U.S EPA, 1997) and sustainable solutions should be taken into account for treating the wastes. PAC is not preferred to be used in comparison with GAC as a recommended method in future for this case because of its poor recovery and high headloss.

Peat

It is a cheap and easy to use material for treatment of aqueous solutions containing heavy metals. The sufficient bed depth of peat is about 0.5 m (Headley, 2066) . The diameter of column is considered to be 35 cm as the same columns used in treatment by GAC in the previous part. The average density of peat is approximately about 150 kg/m^3 (Headley, 2066); the needed volume of peat would be about 0.05 m^3 . It means 7.5 kg of peat is needed for each column. In order to be on the safe side it is assumed that at least two columns and 15 kg of peat are needed. Based on a personal communication (a group using peat for wastewater treatment as a master thesis project at Chalmers), $\frac{1}{4}$ of unsieved peat is achievable as sieved peat. Hence for obtaining 15 kg of sieved peat, 60 kg of raw peat is needed. The price of peat is about 140 SEK/m^3 (personal communication). The cost of 60 kg of unsieved peat would be 56 SEK. But it's just the cost of peat as adsorbent and it needs to have the cost estimation for the whole treatment facility. There is no published cost estimation using peat for treatment of mercury, and it is inevitable to use the same cost estimation used for GAC. It is assumed that the cost of peat is different between two methods (under the item called "the operational cost per cycle"). The flow rate and other parameters are equal for both methods, then the construction cost, electricity consumption and labour cost are all assumed to be the same for peat treatment. The cost of disposal might be different because the spent material would be different, but it is hard to distinguish the cost in this case.

Based on Table 11, the items called "material" and "disposal" (as operational cost per cycle) would be different for peat. Hence the capital cost is estimated to 50,000 SEK (like the one for GAC) and the annual operational cost per cycle would be 2,100 SEK. Due to lack of information about the volume of treated Hg contaminated wastewater before reaching to breakthrough, the changing period of filter is assumed to be every 3 months. This is just an assumption, and obviously if the effluent concentration does not exceed the inlet concentration after 3 months, the changing period will last further. The annual operational cost would be estimated as 8,400 SEK.

Unfortunately no mercury removal percent was found in the literature study. The only value related to adsorption capacity was 82 mg/g obtained in a batch system study (Bulgariu, 2008). Obviously the conditions under batch experiment are totally different compared to the column studies. It is not possible to calculate the amount of treated water per kg of peat as there is no data about breakthrough curve for treatment of Hg contaminated wastewater. That is the reason why it is difficult to estimate how often the peat should be switched.

The optimum pH for treatment of Hg contaminated solution by peat ranging from 5 to 5.5. In order to get the best removal result, pH adjustment might be needed before and after treatment. The costs of chemicals used in pH adjustment were discussed in the previous part and would not be too much in this case. As mentioned before, clogging may cause limited hydraulic charge to the system, so a pre-filter step may be needed. Color-leaching of peat may affect the aesthetic of discharging water from the system. Due to its low hydraulic loading, it's not suitable for treatment of large volume of wastewater but the main advantage of this system is its low capital and operational cost.

7.2 Precipitation/Co-precipitation

In order to be able to use this technique for leachate treatment at the Välen deposit site, some site specific parameters such as pH, initial mercury concentration, flow rate and temperature need to be assessed and compared with the same parameters from the previous studies to know if the technique is applicable to the site or not. The effectiveness of chemical precipitation is dependent on a number of factors as concentration of dissolved metals in the solution, the reagent used, the presence of other metals and pH (U.S. EPA, 2007).

The average pH of inlet flow to the columns at the site is 8.7 while the optimum pH range for the most effective sulfide precipitation in this technique is 7-9. It is obvious that the pH of leachate at site would not affect this type of precipitation. The optimum pH range for the hydroxide precipitation process is 7-11 which proves that this type of precipitation does not work as effective as sulfide type regarding the pH at site.

There are some other competing ions and metals in the leachate affecting the effectiveness of precipitation, presented in the Appendix 5. However it might be possible to overcome the effects of other metals according to Table 3. Based on the presented results in this table, a 58-99.8% mercury removal from chlor-alkali wastewater (including a variety of different metals) in pH ranging from 5.1 to 8.2 was achieved by using sulfide salt following filtration as additional treatment. According to the other results in that table, it is possible to say that pH could be variable depending on the used chemicals and wastewater characteristics. In addition, by using additional treatment methods, it is possible to get the optimum percent removal.

All initial mercury concentrations in previous case studies are much higher than the initial mercury concentration in leachate from Välen deposit (the avg value ≈ 2.4 µg/l). In the theoretical chapter, some cost estimations of different studies were described, but in order to have an appropriate cost estimation of applying this method to Välen deposit site, a cost estimation of sulfide precipitation conducted by Tiravanti, et. al. (1987) (which was not described in the theoretical chapter) was scaled down. The percent mercury removal of the technique following filtration in previous studies has been ranging from 58 to 99.8%.

The method was conducted for 50 m^3/d of wastewater containing initial mercury concentration of 3 mg/l. The flow rate of this study was 10 times higher than the assumed flow rate for (5m^3/d) the Välen deposit site. The only possible estimation, the capital cost and every single item of annual operational cost is scaled down 10 times less than the original estimation. In this way, the scaled down capital cost would be 180,000 SEK ($28,000, 1987 basis). Figure 21 shows the flow diagram of unit operation with scaled down data used for technical- economical analysis.

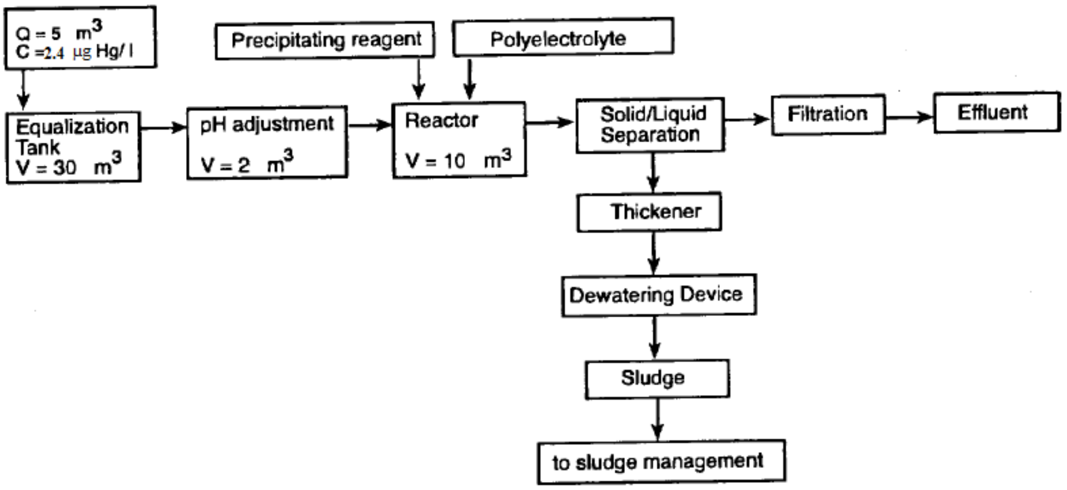


Figure 21. Flow chart of technical-economic analysis (based on the model by (Tiravanti, 1987).

The annual operating costs are presented in Table 12. The total annual operating cost is 58,500 SEK including different items. Sludge management plays an important role in case of cost.

Table 12. Annual operating cost, 1987 basis (based on mercury removal processes from chlor-alkali wastewaters (Tiravanti, 1987)).

Cost item	**Sodium sulfide precipitation**
chemicals	
Precipitating reagent	SEK 300
Polyelectrolyte	1,300
Ferric sulphate	470
Sludge treatment	
Lime	726
Ferric chloride	1,100
Transportation	3,000
Sludge disposal	17,500
Maintenance	5,400
Manpower	13,000
Electric energy	15,700
Total	**58,500**

Regarding the drawbacks of the method as mentioned in the theoretical chapter, it is a technique with difficult functionality. The technique needs rather high labour cost. There is an urgent need for pH adjustment of effluent since a lot of chemicals are used during different steps of this technique.

7.3 Ion exchange and inorganic adsorption

The inlet concentration of unfiltered total mercury measured in the pilot test at Välen was in average 2.47µg/L (10 samples). The filtered inlet mercury concentration (sieved through a 0.45 µm filter) was in average 0.16µg/L which means that 94 % of the total mercury was collected by the filter. To have a pre filter that removes particles is often crucial in case of ion exchange resins and the most resins often removes ionic mercury rather than particle bound mercury. The water at Välen mostly has particle bound mercury, and a pre filtering step seems relevant if using ion exchange as a method.

The resins SIR-200 and Keyle:X were able to remove mercury down to under 0.05 µg/L for contact times at minimum 1 min in the short term test. The guideline value for Hg used in this report is 0.07 µg/L which means that these two resins could remove mercury down to this level. In case of SIR-200, even a contact time of 0.33 min is possible to be under 0.07 µg/L according to Hollermann (1999). Also these two resins showed good performances in the long term see Figure 6. The effluent concentration was under the 0.07 µg/L limit at some occasions but would most likely been under the level more often for longer contact times (lower SFR).

Since the removal efficiency according to the short term study shows to increase with lower SFR one can assume that the lowest SFR (longest EBCT) should be chosen. If so, 1.85 and 7.7 minutes should be suggested for Keyle:X and SIR- 200 respectively (according to Table 5).

It is assumed that more water should be collected to the sludge well prior to any treatment step, perhaps 5 m^3/day. This means that a continuous flow of 3.5 L/min is possible to be let to an ion exchange system. This flow together with an EBCT of 7.7 minutes (in case of SIR- 200) will require a resin bed volume of 27 L. For a Keyle:X resin column only 6.5 L would be needed. The relatively short contact times needed with this technique means smaller column volumes which results in a relatively low cost for columns.

These two resins are different when it comes to the chlorine concentration in the water. Manufactures for the Keyle:X resin suggests to pre-treat the water with chlorine, hypochlorite or chlorine dioxide to 1-2 mg/L in order to be sure that the mercury occurs as ions in the solution (Klasson, 1998a), while all chlorine and other oxidizers must be removed prior to SIR- 200 resin since it otherwise oxidizes the functional groups of this resin. At Välen the total chloride concentration varies from 35- 200 mg/l in the inlet but the chlorine concentration is unknown.

Table 13 shows the total concentrations of elements in the leachate at Välen as well as the capacity for these elements for the resin SIR 200. Metals with lower selectivity occur in much higher concentrations compared to mercury, and they might be more easily chelated by the active groups.

Both these resins solely treat dissolved cations including mercury (Hg^{2+}). This is unfortunate since it turns out that the metals occur mostly bound to particles at Välen. This is why a filtering prestep is recommended.

Table 13. The equilibrium capacities of the SIR- 200 resin for some metals and the total concentrations of the same elements in the leachate at Välen deposit site.

Metal cation	**Equilibrium Capacity, eq\l (g/l)**	**Minimum pH required**	**Inlet concentrations of elements at Välen, unfiltered and (filtered) [µg/L]**
Mercury (Hg^{2+})	1.2 (120)	2	2.47 (0.16)
Silver (Ag^{+})	1.2 (129)	2	-
Copper (Cu^{2+})	1.1 (35)	3	43 (6.6)
Lead (Pb^{2+})	0.5 (52)	4	0.52 (0.2)
Cadmium (Cd^{2+})	0.5 (28)	4	0.05 (0.05)
Zinc (Zn^{2+})	0.3 (10)	5	8.26 (2.45)
Nickel (Ni^{2+})	0.2 (6)	5	58 (53.8)

SIR-200 can be regenerated while Keyle:X is recommended not to. Regenerations can be seen as an advantage or as a disadvantage. If regenerating the resin it does not have to be replaced as often and virgin material is saved. On the other hand the non-generable resins often have good capacities over a longer period and are according to the manufacturer not profitable to be regenerated. Further, if not regenerated, chemicals are saved as well as cost and work for handling the residues. Considering functionality as a valuable parameter at Välen, it makes sense to use a non-generable resin.

The cost for an ion exchange system mentioned in the theoretical part of this report contained several pre steps including a mechanical pre filter and an activated carbon column for removing organic substances. Since the leachate contains large amounts of total solids but also TOC/DOC it might be wise to install both a filter that can trap particles and solids and a pre step to adsorb organic substances in order to let the ion exchange resin to be efficient and to avoid problems of clogging.

The Price for Keyle:X resin material is according to (Klasson, 1998a), about 802 SEK/l but according to (He, 2010) 222 SEK/l. SIR- 200 is 83 SEK/l according to (He, 2010). The price for TP 214 was according to *Eurowater* 271 SEK/35 l of resin = 7.7 SEK/l which is less. Probably the price for SIR- 200 and also Keyle:X would be lower if buying larger quantities and depends from where it is bought.

Since the column suggested by *Eurowater* can treat up to 800 L/day (13.3 L/min) with a cost of 20700 SEK, a column that can treat up to 3.5 L/min can be assumed to cost around 5000 SEK based on scaling of the cost. The pump (7780 SEK) estimated, could in the same way be scaled to 2050 SEK. The cubicle, tank and pre filter are consider to be the same.

The operating cost is highly dependent on the cost of replacement. The best way of estimating the replacement frequency is to make a pilot study where breakthrough is reached.

Keyle:X is approximately 3 times more expensive than SIR- 200 per liter of resin, but the quantity of Keyle:X required is about 4 times less due to its ability to operate at higher SFR. The operating cost will therefore mostly depend on the time to breakthrough which means time before regeneration in case of SIR-200 and switching resin bed in case of Keyle:X.

Capital cost

Installation: 15000, mechanical pre filter: 20000, columns: (5000*3), tank: 14 600, cubicle: 6 500 and pump 2050 = 73150 SEK.

O&M

Chelating resin

Based on the shortest recommended SFR and a flow of 5 m^3/day, 6.5 L bed volume of Keyle:X is needed. The price of Keyle:X is 222 SEK/L, hence 1443 SEK/resin bed. If just assuming a change out period of 3 weeks, then the resin bed should be switched approximately 18 times/year. The cost of chelating resin material is then 25974 SEK annually.

Resin for 2- charged ions

Lewatit TP 207 as suggested by *Eurowater* has a cost of 3.2 SEK/L. Assuming a bit longer required contact time (10 min) gives a bed volume of 50 L. With a change out period equal to that of the chelating resin the annual cost would be 2880 SEK.

GAC filter for organic material

Assuming the same contact time as in the pilot study i.e. 30 minutes gives with the estimated flow a bed volume of 105 L. The GAC given by *Eurowater* (08 SUPRA) costs 1880 SEK/50 L/ = 3948 SEK/GAC bed. If assuming a change out period of 5 weeks this means 10 times per year and a total material cost of 39480 SEK/year.

Sand

The sand price is in average 5 SEK/L based on the price from *Eurowater*. If assuming a quantity approximately half that of the GAC/resin then 3+ 25+ 55 L ≈ 85 L is required. If switching the sand every 4th week (assumption) then the yearly cost is 5525 SEK.

The total annual cost is then 25974+ 2880+ 39480+ 5525= 73859 SEK/year.

7.4 Biological treatment

7.4.1 Phytoremediation

Phytoremediation is less sensitive to fluctuations in amount of water at the site and in concentrations and does not require any pre collection of the water. Most phytoremediation processes though require a water rich soil for growth and for easier access to contaminants. The contaminants are spread out over a large area and because little water is reached to the sludge well, this technique could be a good option. The plants will most likely neither worsen the esthetical view since there already are plants at the site.

A negative aspect is the potential emission of elemental mercury in case of phytovolatilisation. At Välen the metal contaminated deposit is protected for a reason, the mercury and other pollutants should not be spread to neighbouring places. This can be solved by genetically engineered plants which both are more tolerant, effective and can store the metals in their tissue followed by harvest. This technique seems really promising due to its eco friendliness but is still on a research level and to purchase modified plants might be difficult.

Besides the potential harvest of plants and a comprehensive site investigation prior to the operation it is a relatively passive method which also creates little residues at the site. The process is though very slow.

To use this method could also be problematic when it comes to regulation; would it be legal to operate it? Modified plants have as mentioned harder to adopt in the wild and the technique is maybe not yet fully understood. The technique also requires proper conditions at the site. Temperature and pH must be satisfied enough. Nutrients must be available, which seems to be the case if looking at the data collected.

The cost for phytoremediation at the site of Välen cannot easily be estimated as the type of phytoremediation that would be the best alternative and all costs involved are hard to assess. However the cost estimated by US. EPA (2000) for phytoextraction is $6700 for 12 acres (4.8 hectares), approximately the same size as Välen (5 hectares). The price for 4.8 hectares did not consider the depth which makes it hard to know the price per cubic meter. The depth at Välen is 3 meters and the root system of most hyper accumulating plants might be too short to be appropriate at this site. For phytostabilization the price was estimated to $1 per cubic meter of soil. Considering 3 meters in depth to be contaminated and the 5 hectare area this means 150 000 m^3. The total price is then $150 000= 983 300 SEK ($1= 6.55 SEK 2011-08-11).

7.4.2 Bioaccumulation

The use of real bacteria (or other microorganisms) actually transforms the metal species. As in the case of phytoremediation the bacteria needs to be engineered in order to store the transformed metal species so not to volatile e.g. elemental mercury. Many different systems are available and proven efficient for bioaccumulation but in the case of advanced engineered bacteria for specific metals e.g. mercury, little information of where to purchase or the cost are available.

When it comes to functionality, this technique is one of the most difficult to operate since the living bacteria need almost perfect conditions to operate. The removal efficiencies are not as good as the other techniques alone.

7.4.3 Biosorption

Biosorption is a relatively cheap method and very many various materials are available e.g. dead plants, bacteria, fungi or to reuse biological products. One factor that makes this technique interesting at Välen is its eco friendliness and availability. Materials can often be found locally and the use of spent/dead materials saves the production of virgin materials and avoids the production costs. The functionality is another; it does not require the same perfect condition and monitoring as in bioaccumulation and can be operated in many different ways e.g. in columns or on carriers in water tanks.

Biosorption is to prefer at Välen over bioaccumulation for various reasons. According to the literature search, biosorption is more easily maintained and are more versatile compared to bioaccumulation. It is also less sensitive to fluctuations in temperature and pH. Biosorption materials like the nonviable bacteria Bacillus sp. are though somewhat sensitive to higher pH and works better below 6. The colder temperature at Välen should not be a problem.

The relatively low metal concentrations at Välen compared to in many former studies should matter less in case of Biosorption where often the efficiency goes up with decreased initial concentration. Bioaccumulation is suitable better for higher concentrations of mercury.

Bioaccumulation is also sensitive to chlorine, which might be another problem at the site. One advantage with bioaccumulation is that it can be more selective. But since there is a wide range of pollutants in the leachate water at Välen classified as hazardous to the environment it is good with a material able to treat a large variety of pollutants.

Using fixed- bed (column) Biosorption solely could be a bad option at Välen since it works almost solely for dissolved metals and not particles. A filtering pre step could be installed before a column system or Biosorption in a fluidized bed configuration could be used instead.

When it comes to space requirements for these techniques, Biosorption could reasonably need less space since non-viable organisms neither grow nor require additional aeration.

The Biosorption material on the other hand has to be replaced and spent material must be deposed of as hazardous waste.

The choice of material is of importance where a trade- off might be necessary between efficiency and cost. There are both cheap and expensive Biosorption materials depending on if they are naturally occurring/by-products or manufactured/specially propagated biomass. The latter ones are often more effective but more expensive. No cost estimation has been found during the literature study for Biosorption but the price should be near the cost for a GAC system but with a cheaper material cost.

7.5 Membrane filtration

When using membrane filtration it is crucial to specify what metal species to be removed and to know the metal speciation in the water. If the water contains a large fraction of free cations which are desired to be removed, then the pore size of the membrane media needs to be smaller which is more expensive. Instead a pre-step like precipitation that converts the dissolved species into colloidal particles can be installed. These are then more easily removed by a larger pore size filter. There is obviously not a large fraction of the mercury available neither as free cations nor as mercury chloride or methyl mercury which makes the choice of a larger pore size possible and hence this technique seems to be an option. The methyl mercury occurs far over the guideline value, and free occurring methyl mercury would pass an Ultra- and Micro filter. If it is considered important to trap these smaller mercury species (even though they are in minority) either nano filtration or a combination of an Ultra- filtration filter with a pre step like precipitation is required.

The price for a membrane filtration system including precipitation was given in the theoretical part in this report, which was based on a water flow of 200 m^3/day. The cost for the full scale plant was 1 234800 SEK (£1= 10.29 SEK 2011-07-16) as capital cost, 1.75 SEK/m^3 as O&M excluding electricity which additionally was 0.67 kWh/m^3. With a 5 m^3/day flow (1825 m^3/year) the O&M would be 3188 SEK/year and the electricity 1222 SEK/year (1 SEK/kWh assumed). Notable is that the O&M cost is valid for a water flow of 200 m^3/day and that the price per cubic meter most likely increases with lower flows. Also the electricity consumption seems fairly low. The capital cost on the other hand might be slightly cheaper due to a smaller equipment cost. The prices are not possible to scale up since the relationship between flow and costs are not linear. The total cost is hence 1,234800 SEK + 4400 SEK/year as O&M.

This treatment method will require a relatively large facility not least if including a necessary pre step to avoid having a nano filtration or reverse osmosis system. Besides having a possible pre-treatment step and the primary filtering step, the system also must include either a back circulation line or a dewatering step for the reject stream and perhaps also a post treatment step for the permeate if this not fulfils the effluent criteria. It hence has a large land requirement and should be kept inside, to avoid noise etcetera. This is something that might disturb the recreational value at the site and be ostentatious for people living nearby. The residues in these systems are the solid filter cake that builds up on the inside of a cross flow system or on the surface of the membrane in case of dead- end mode. Also there will be the concentrated sludge alternatively a fairly solid waste of the concentrated reject stream. If having precipitation as a pre step this of course ads additionally waste. To handle the waste including collection, transportation and deposition is probably a cost that was excluded in the cost. Concerning the necessary labour at site to monitor the process and a technical expertise means this method is one of the most challenging ones.

8 Comparison of techniques

The techniques will here be evaluated and compared based on some predefined criterion. These are *functionality*, *eco friendliness*, *cost* and *efficiency*. The criteria *cost* and *efficiency* has quantitative units but *eco friendliness* and *functionality* are judged qualitatively. The idea is to make a qualitative assessment where scores will be set under each criterion. *Social aspects* were considered important prior to the comparison. The social part would then include mainly parameters connected to human senses like smell, noise and look. The different techniques are more or less the same, assuming all of them except phytoremediation, can be kept inside a container. The effluent water and/or residues will for all methods contain mercury and other heavy metals and there will probably be a smell from the site if going near the facility. The *social aspect* is for these reasons excluded as comparison criteria in the comparison part.

In case of cost, both capital cost and O&M will be given separately with the unit Investment cost (SEK) and SEK/year for operation. Functionality refers to the easiness of maintenance and operation (unit less). Eco friendliness includes the residues/emissions created during operation and the materials used (unit less). The efficiency is the removal capacity of mercury in terms of % removal or mg/g uptake capacity.

Table 14. Summary of parameters for each technique from the site specific part.

Methods	**Adsorption**		**Precipitation** **(Sulfide.P)**	**Membrane filtration**	**Ion Exchange**	**Biosorption**	**Bioaccumulation**	**Phytoremediation**
Criterion	**GAC**	**Peat**						
Cost								
Capital (SEK)	50,000*	50,000*	180,000	1,234800	73,150	Close to peat	NA (fairly high)	491,650 (half of 983,300)
Annual O&M (SEK/year)	22,600*	8,400*	58,500	4,400	73,859	Close to peat	NA (high)	491,650 (half of 983,300)
Eco friendliness								
Residuals	Ash & emission from reactivation of GAC	Spent peat-ashes and emission from incineration	Chemical-toxic sulfide sludge	Filter cake, reject stream & washing	Spent resins & washing or chemical from regeneration	Spent material-chemicals for regeneration or incineration	Microorganisms incineration	Perhaps volatized Hg Ash from incinerated harvested plants
Materials	Semi friendly	Friendly	Not friendly	Not friendly	Not friendly	Semi friendly	Friendly	Semi Friendly
Efficiency (%)	99.8	81.97 (mg/g)	58-99.8	98.5	94 or 80	91.9	95	NA
Functionality	Easy-moderately	Easy-moderately	Hard	Moderately-hard	moderately	Easy-moderately	Very Hard	moderately

*The cost of GAC is based on 2001$ and for Sulfide precipitation based on 1987$.

Table 14 summarizes the information given in the site specific part. The cost information have been gathered from various pilot or full scale projects and the cost for the case study Välen is estimated (sometimes scaled up) to fit the water flow at Välen. As also discussed in the site specific part under each technique, it has been hard to estimate the cost fairly and trust worthy. Different costs are based on different treatment trains, conditions and do not include the same cost parameters. Some do contain labor, land requirements and disposal while some are not. Sometimes the cost is valid for a specific flow interval if presented per cubic meter or as a yearly cost. The costs are thus roughly estimated as good as possible for the comparison. Efficiencies are also gathered from different literature reports and articles which have different conditions and treatment facilities and cannot possibly be adopted straight of for the site of Välen, but gives an idea of the method´s efficiency. The values refer to the removal of mercury only.

The *functionality* has been judged with easy-moderately, moderately, moderately-hard, hard and very hard and refers to the installation but mostly to the operation and maintenance when it comes to time and expertise requirements. For *eco friendliness* the *materials* are judged based on the levels friendly, semi friendly and not friendly and refer to if the treatment materials used are eco friendly during operation and in manufacturing. About *residuals* the kind of residuals are mentioned. The residuals often differ from one technique to another. Actually depending on the residual management for each technique, all possible potential adverse effects of each technique have been taken into account. There might be one or more ways of disposal for residuals of each technique.

About the *cost* criteria, for phytoremediation, the price refers to a total cost including both capital and O&M. For simplicity the price has been divided in two where one half belongs to capital and the other half to O&M for the comparison. No cost was available for Bioaccumulation, but for its capital cost it has been placed in between the cost for phytoremediation and membrane filtration. The O&M cost is according to literature very expensive and is therefore estimated by the authors to be the most expensive technique. For Biosorption the price was neither available but are reasonable comparable to peat and are therefore estimated to have the same capital cost and O&M cost.

For the comparison no weighting is done, hence no criteria are more or less important and heavier weighted. The reason for this is that the authors themselves cannot judge the priorities in criteria and there are no specific requests for any weighting to be done. The results can therefore be changed easily by an implementation of weighting factors e.g. from 0- 100 %. The scores are set based on the number of different results under each criterion and that the highest score is 8 based on the number of techniques. As seen in Table 15, for e.g. *materials* there is 3 different results, friendly, semi friendly and not friendly. The given scores are hence 2.66 (8/3), 5.33 ((8/3)*2) and 8 ((8/3)*3). For *efficiency* there is 8 different results and the scores are then even distributed from 1-8.

Table 15. The comparison of techniques based on the predetermined criterion. No weighting of criteria is done.

Methods	**Adsorption**		**Precipitation (Sulfide.P)**	**Membrane filtration**	**Ion Exchange**	**Biosorption**	**Bioaccumulation**	**Phytoremediation**
Criterion	**GAC**	**Peat**						
Cost								
Capital	8	8	5.33	1.33	6.66	8	2.66	4
Annual O&M	5.71	6.86	4.57	8	3.43	6.86	1.14	2.29
Eco friendliness								
Residuals	6.4	6.4	1.6	4.8	3.2	3.2	8	6.4
Materials	5.33	8	2.66	2.66	2.66	5.33	8	5.33
Efficiency	8	2	3	7	4	5	6	1
Functionality	8	8	3.2	4.8	6.4	8	1.6	6.4
$\sum$	41.44	39.26	20.36	28.59	26.35	36.39	27.4	25.42

No efficiency data was found for Phytoremediation, why the lowest score (1) was given in this criterion. Ordinary hyper accumulating plants are believed to be less efficient compared to the other techniques studied in this report. For peat, no % removal data was given in literature, only in mg/g. It was therefore hard to estimate and the score 2 was given.

GAC as technique was given to total highest score of 41out of 48. The overall scores are seen in Table 15. The outcome of this table as mentioned should only be seen as guidance for selection of a technique that can be applicable at Välen. The final outcome might differ with other criterion and implementation of weighting.

9 Conclusions and recommendations

Conclusions

The leachate flow measurements made during the period 11th May to 15th June was in average 0.074 L/min (0.1 m^3/day). This flow is considered to be low and less than expected. This flow is too low to be let directly to any treatment facility in order to maintain an enough large continuously flow. A tank prior to a treatment facility can be installed to collect the water but due to the low inflow to the sludge well the water volume in the tank will not be sufficient to serve the facility with water. All techniques studied with an exception for phytoremediation would require a larger water inflow to the sludge well.

The field experiment with activated carbon columns showed efficient removal for many elements in the leachate including mercury. Breakthrough for total unfiltered mercury was unfortunately not reached. This is mainly due to the lack of water available during this experiment. The tank could not be filled up continuously and hence the columns did not receive enough water in order to hold many bed volumes of water. Breakthrough would likely be reached within a short time period if more water could be collected and with a higher regulated flow rate through the columns.

The average effluent concentration for all dissolved elements except Cl^-, Na, Al, Cd, Pd, Zn and Hg (filtered) were above their guideline values during the experiment. Good removal efficiency by the GAC for many elements was not enough due to high inlet concentrations and the sometimes strict guideline values. Better results would probably be reached with a better pre filter and/or more columns in series. Further column studies are needed with different configurations and not least more water to investigate the true capacity of this technique at Välen.

All considered techniques were compared to each other based on a numbers of criteria. Such those criteria are cost, eco-friendliness, efficiency and functionality. Each technique was given score based on its advantages and disadvantages regarding the criteria. The GAC method was chosen as the best technique and got the highest possible score. The second best technique was chosen as treatment by peat and the third one was considered as biosorption. Although the possibility of any error or mistake in terms of comparison of techniques (based on criteria mentioned above) is not dismissed since the performance and efficiency of each technique may differs under different conditions.

Recommendations

A more in depth site investigation at Välen is recommended in order to get a better understanding of how the site is built up and where the leachate water might leave the deposit site. After that one can see possible improvements of how to protect the deposit site and how to collect more leachate water towards the sludge well. This is to avoid the leachate to leave the site untreated and to collect more water in order to make any treatment facility on site meaningful.

To continue to measure the incoming water to the sludge well is also recommended in order to get a better estimation of the yearly inflow and to see seasonal fluctuations of the flow. This operation is easy and can be done as during the field experiment by just measuring the water level increase in the sludge well. The sludge well can contain approximately 3 m^3 of water, and with an inflow of 0.1 m^3/day it would be filled up after about 30 days. The measurements can tentatively be done every 3rd or 4th week.

Further column studies can be done with GAC (perhaps the same as used by the authors) when more water is collected. A flow of 0.75 l/min as predetermined by the authors or perhaps larger can be tested for a longer period to make sure breakthrough is reached. This results will be the base for calculating the proper dimensions and knowing the change out period of the GAC and hence the quantity of needed material and costs. Since it was noticed during the experiment that the first column got easily clogged, a better pre filter than the sand used in this study and/or frequently backwashing is needed. Preferably an automatically backwashing mechanism built in the column is recommended to avoid doing it manually several times per week (if having more water).

At the same time, to test other adsorption materials e.g. peat might be interesting as an comparison with GAC to see which of these two that are more sustainable i.e. cost effective and efficient in longer studies. A laboratory (smaller) scale test might be done before testing this in field to better investigate the sorption capacities and breakthrough in smaller columns and a variety of concentrations and SFR of the water.

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Appendices

Appendix 1- Chelating resins

SIR- 200

SIR-200 manufactured by Resintech is a macroporous cation exchange resin made of polystyrene/DVB with thiol functional groups which has chelating properties for mercury and other noble metals as divalent cations (II+). The order of selectivity follows: Hg>Ag>Cu>Pb>Cd>Ni>Co>Fe>Ca>Na

It has the ability to reduce mercury ions to very low levels in presence of other heavy metals (Incorporation). For more information see (Resintech Incorporation, 2011).

Purolite S920

Purolite S920 from Purolite Company is also a macroporous cation exchange resin made of polystyrene/DVB but with thiouronium as functional group. It is largely selective for mercury but also for gold, platinum and palladium(Company, 2010).

For more information see (Purolite company).

Amberlite GT-73

Amberlite GT-73 previously known as Duolite GT-73 is a trademark from Rohm & Haas Company owned by Dow Chemicals Company. It is a polystyrene/DVB resin with thiol functional groups with a high preference for mercury but effectively removes also silver, cadmium, copper and other heavy metals(Company, 2001). It can be regenerated with concentrated hydrogen chloride solution (Company, 2001).

According to personnel at Dow Chemicals the Amberlite GT-73 has recently been replaced by Ambersep GT- 74, a new resin with similar properties to that of GT-73 with an order of selectivity as follows: Hg>Ag>Cu>Pb>Cd>Ni>Co>Fe>Ca>Na. For more information see (Rohm and Hass Co, 2006).

Ionac SR-4

Ionac SR-4 from Lanxess Sybron Chemicals Incorporation is unfortunately absolete and out of production. It was a weakly acidic cation exchanger based on aliphatic thiol functionality tied to a polystyrene/DVB backbone that was highly selective for mercury and silver. It enables to remove very low quantities of mercury from waters with capacities as high as 90-180 g/l (Incorporation, 2003) Another resin that today has similar properties as the Ionac SR-4 is LewatitMonoPlus TP214 from Lanxess. For more information see (Syborn Chemicals Inc. A Bayern Company, 2003).

LewatitMonoPlus TP214

This resin is a macroporous polystyrene/DVB chelating resin with thiourea as functional group(Lanxess, 2005). The thiourea is in the form of isothiourea with the sulfhydryl (-SH) (right side in Figure 23) which makes it highly selective for mercury, but also platinum, silver and gold(Lanxess, 2005). For more information see (Lanxess Energizing Chemistry, 2011).

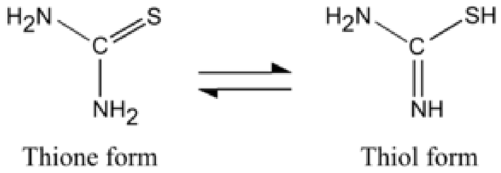


Figure 23. Thiourea in the Thione and Thiol (isothiourea) form.

Keyle:X

Keyle:X is patented by Solmetex and is a thiol-based sorbent which selectively binds mercury with a very high total capacity of 3,4 eq/L (Hollermann, 1999) referring to Solmetex. Keyle:X uses a combination of chelating and affinity chromatography to speed up the metal separation and the capacity for metals extraction(Solmetex, 2011). According to (Hollermann, 1999) further referring to Solmetex, Keyle:X cannot be regenerated. With a high practical recommended flow rate of 1, 07 BV/min (the same as for GT-73) a short contact time is required for efficient use(Hollermann, 1999). For more information see (Hollermann, 1999).

Appendix 2- Parameters analysed and their Instruments

Table 7. The analysis instruments and their accuracy are shown. For the metals analyzed at ALS laboratory, the accuracy shows different values for every analysis occasion and differs for all metals. One accuracy (%) cannot therefore be chosen.

Parameter	**Instrument**	**Accuracy (%)**
In field		
Temperature (°C)	multi 350i	
pH	-“-	±0.004
Conductivity (mS/m)	-“-	±0.5
DO (%)	-“-	±0.5
DO (mg/l)	-“-	±0.5
At Chalmers laboratory		
NPOC (mg/l)	New TOC device	±20
Diss. NPOC (mg/l)	New TOC device	±20
Tot N (mg/l)	New TOC device	±20
Diss. N (mg/l)	New TOC device	±20
Cl^- (mg/l)	Fast method	
Tot Solids (mg/l)		
External laboratory (ALS)		
Analysis package V3a		
Al (mg/l)	E,F,H	
As (mg/l)	E,F,H	
Ba (mg/l)	E,F,H	
Ca (mg/l)	E,F,H	
Cd (mg/l)	E,F,H	
Cr (mg/l)	E,F,H	

Co (mg/l)	E,F,H	
Cu (mg/l)	E,F,H	
Fe (mg/l)	E,F,H	
Hg (unfiltered) (µg/l)	F	
Hg (filtered) (µg/l)	F	
K (mg/l)	E,F,H	
Mg (mg/l)	E,F,H	
Mn (mg/l)	E,F,H	
Na (mg/l)	E,F,H	
Ni (mg/l)	E,F,H	
Pb (mg/l)	E,F,H	
Zn (mg/l)	E,F,H	
Additionally added		
Methyl-Hg (ng/l)		
Tot- P (mg/l)	E,F,H	

E= ICP-AES
F= AFS
H= ICP-SFMS

Appendix 3- Detection limits for parameters in comparison with EQS

Table 17. Detection limits for parameters in comparison with EQS.

Parameter	Unit	Detection limit	Lowest value	EQS
NPOC	mg/l	-	14	<4
Tot N	mg/l	-	390	<0,3
P - tot	mg/l	0,01[a]	1,63	<0,0125
Al	µg/l	2[a]	220	_ /500
As	µg/l	1*[a]	6,1	<0,4
Ba	µg/l	0,2[a]		
Ca	µg/l	200[a]	51000	_/100000
Cd	µg/l	0,05**[a]	<0,02	<0,01
Co	µg/l	0,05[a]		
Cr	µg/l	0,5[a]	6,2	<0,3
Cu	µg/l	1[a]	2,1	<0,5
Fe	µg/l	4[a]	460	500
Hg (unfiltered)	µg/l	0,02[a]	0,21	0,07
Hg (filtered)	µg/l	0,02[a]	<0,1	<0,05
Methyl-Hg	ng/l	0,1[a]	30	<10
K	µg/l	500[a]	570	_ / 12000
Mg	µg/l	90[a]		
Mn	µg/l	0,2[a]	13	_ / 300
Na	µg/l	120[a]	2600	100000/_
Ni	µg/l	0,5[a]	55	<0,7
Pb	µg/l	0,2[a]	<0,15	<0,2
Zn	µg/l	2[a]	5	<5

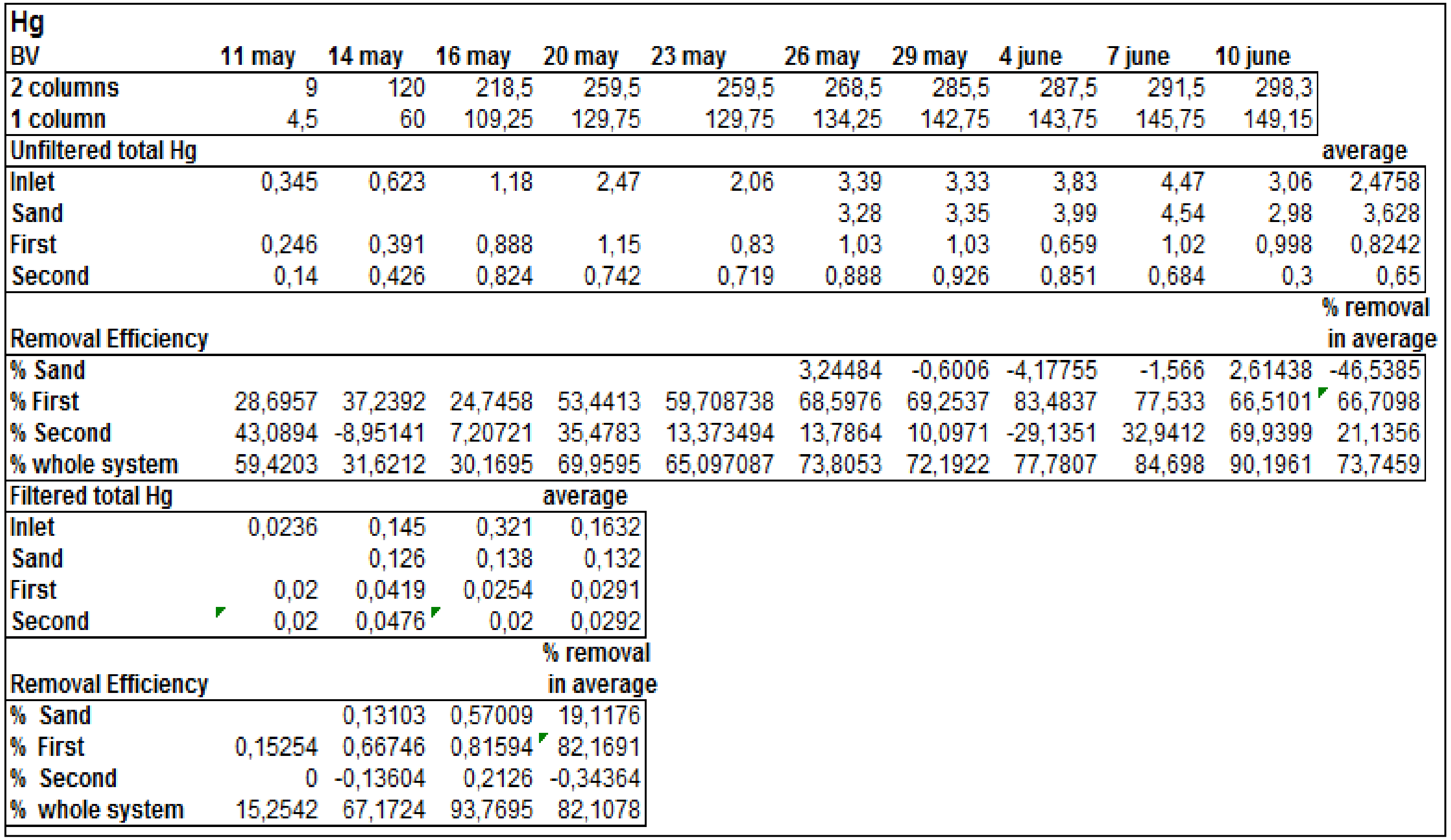
* For high concentrations of chloride the detection limit will be increased.

** For high concentrations of molybdenum the detection limit will be increased.

[a] Detection limits are gathered from : (ALS Scandinavia, 2011).

Appendix 4- The analysis data for all substances

The table shows measured concentrations of mercury (Hg) in the inlet water expressed in [mg/l] (untreated water from sludge well) and after the sand filter, 1 and 2:nd column respectively. The table also shows the removal efficiency over each column and over the whole column system (in %).



Hg											
BV	11 may	14 may	16 may	20 may	23 may	26 may	29 may	4 june	7 june	10 june	
2 columns	9	120	218,5	259,5	259,5	268,5	285,5	287,5	291,5	298,3	
1 column	4,5	60	109,25	129,75	129,75	134,25	142,75	143,75	145,75	149,15	
Unfiltered total Hg											average
Inlet	0,345	0,623	1,18	2,47	2,06	3,39	3,33	3,83	4,47	3,06	2,4758
Sand						3,28	3,35	3,99	4,54	2,98	3,628
First	0,246	0,391	0,888	1,15	0,83	1,03	1,03	0,659	1,02	0,998	0,8242
Second	0,14	0,426	0,824	0,742	0,719	0,888	0,926	0,851	0,684	0,3	0,65
Removal Efficiency											% removal in average
% Sand						3,24484	-0,6006	-4,17755	-1,566	2,61438	-46,5385
% First	28,6957	37,2392	24,7458	53,4413	59,708738	68,5976	69,2537	83,4837	77,533	66,5101	66,7098
% Second	43,0894	-8,95141	7,20721	35,4783	13,373494	13,7864	10,0971	-29,1351	32,9412	69,9399	21,1356
% whole system	59,4203	31,6212	30,1695	69,9595	65,097087	73,8053	72,1922	77,7807	84,698	90,1961	73,7459
Filtered total Hg				average							
Inlet	0,0236	0,145	0,321	0,1632							
Sand		0,126	0,138	0,132							
First	0,02	0,0419	0,0254	0,0291							
Second	0,02	0,0476	0,02	0,0292							
Removal Efficiency				% removal in average							
% Sand		0,13103	0,57009	19,1176							
% First	0,15254	0,66746	0,81594	82,1691							
% Second	0	-0,13604	0,2126	-0,34364							
% whole system	15,2542	67,1724	93,7695	82,1078							

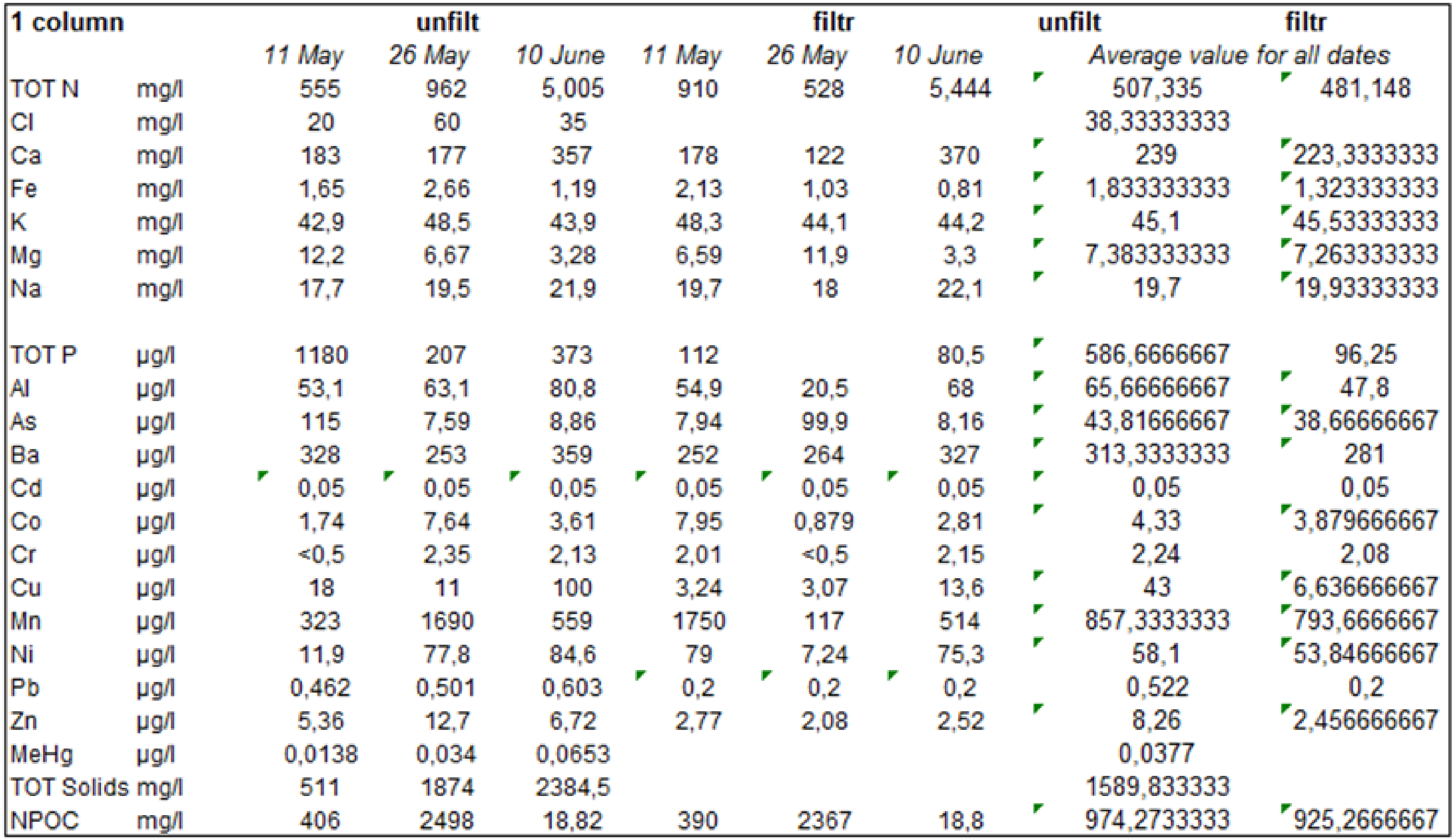
The measured concentrations of different substances in the inlet water (untreated water from sludge well).

Inlet	**unit**	**unfilt**			**filtr**			**unfilt**	**filtr**
		11 May	*26 May*	*10 June*	*11 May*	*26 May*	*10 June*	*Average value for all dates*	
TOT N	mg/l	434	1413	10,54	441	1341	10,51	619,18	597,5033333
Cl-	mg/l	35	60	200				98,33333333	
Ca	mg/l	235	420	606	229	344	585	420,3333333	386
Fe	mg/l	6,18	6,99	3,7	2,94	0,403	2,74	5,623333333	2,027666667
K	mg/l	43	55,8	60,2	44,1	55,5	60,4	53	53,33333333
Mg	mg/l	11,4	2,37	0,9	11,3	2,3	0,887	4,89	4,829
Na	mg/l	17,4	19,4	20,8	17,6	19,5	20,8	19,2	19,3
TOT Hg									
TOT P	µg/l	838	257	12,96		131	158	369,32	144,5
Al	µg/l	192	625	771	162	566	727	529,3333333	485
As	µg/l	4,34	9,73	11,6	4,6	11,5	11,7	8,556666667	9,266666667
Ba	µg/l	141	304	487	139	270	554	310,6666667	321
Cd	µg/l	0,05	0,0597	0.05	0,05	0,05	0,0626	0,0597	0,0626
Co	µg/l	8,19	16,7	16,3	7,32	15,2	15,9	13,73	12,80666667
Cr	µg/l	6,54	35,6	23,7	7,52	21,4	23,9	21,94666667	17,60666667
Cu	µg/l	6,32	8,19	25,4	1	1,27	1,47	13,30333333	1,37
Mn	µg/l	1590	63,3	36,75	1540	16,5	17,3	563,35	524,6
Ni	µg/l	247	754	18,82	237	721	760	339,94	572,6666667
Pb	µg/l	0,34	2,56	39,31	0,2	0,353	0,55	14,07	0,4515
Zn	µg/l	14,8	66,1	37,98	11	44	24,5	39,62666667	26,5
MeHg	µg/l	0,0486	0,22	0,236				0,1682	
TOT Solids	mg/l	1467,5	5444,5	8004,5				4972,166667	
NPOC	mg/l	711	4783	39,7	745	4474	39,31	1844,566667	1752,77

The measured concentrations of different substances after the sand filter.

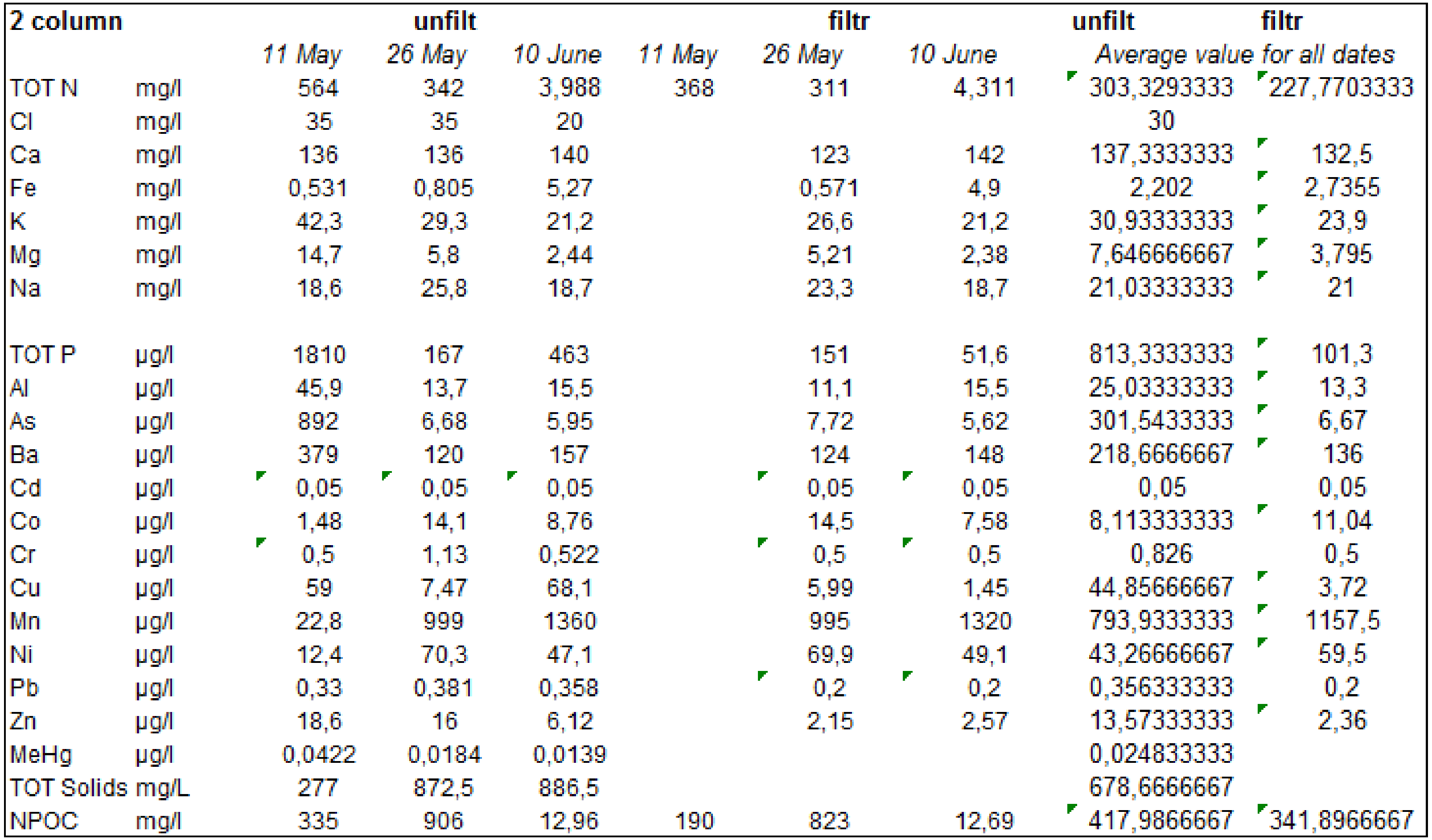
Sand		Unfilt		Filter		Unfilt	Filter
		26 May	*10 June*	*26 May*	*10 June*	*Average value for all dates*	
TOT N	mg/l	1014	9,714	913	10,43	511,857	461,715
Cl-	mg/l	60	100			80	
Ca	mg/l	421	604	587	360	512,5	473,5
Fe	mg/l	5,76	3,83	2,93	0,416	4,795	1,673
K	mg/l	53,9	61,1	59,5	56,1	57,5	57,8
Mg	mg/l	4,83	1,16	1,12	4,92	2,995	3,02
Na	mg/l	19,7	21	20,7	20,3	20,35	20,5
Hg	µg/l	3,28	2,98	0,138	0,126	3,13	0,132
TOT P	µg/l	257	610	153	122	433,5	137,5
Al	µg/l	383	661	611	344	522	477,5
As	µg/l	8,75	11,4	12,1	11,8	10,075	11,95
Ba	µg/l	313	557	530	300	435	415
Cd	µg/l	0,131	0,05	0,05	0,05	0,131	0,05
Co	µg/l	20,2	17,6	17,4	18,6	18,9	18
Cr	µg/l	25,9	23,6	23,3	18,6	24,75	20,95
Cu	µg/l	12,5	357	13,2	3,62	184,75	8,41
Mn	µg/l	193	54,9	47,1	71	123,95	59,05
Ni	µg/l	715	764	753	734	739,5	743,5
Pb	µg/l	4,15	2,38	0,522	0,403	3,265	0,4625
Zn	µg/l	102	50	44,8	72,5	76	58,65
MeHg	µg/l	0,237	0,215			0,226	
TOT Solids	mg/l	5405	7801			6603	
NPOC	mg/l	3433	36,75	3073	37,98	1734,875	1555,49

The measured concentrations of different substances after the first column.



1 column		**unfilt**			**filtr**			**unfilt**	**filtr**
		11 May	*26 May*	*10 June*	*11 May*	*26 May*	*10 June*	*Average value for all dates*	
TOT N	mg/l	555	962	5,005	910	528	5,444	507,335	481,148
Cl	mg/l	20	60	35				38,33333333	
Ca	mg/l	183	177	357	178	122	370	239	223,3333333
Fe	mg/l	1,65	2,66	1,19	2,13	1,03	0,81	1,833333333	1,323333333
K	mg/l	42,9	48,5	43,9	48,3	44,1	44,2	45,1	45,53333333
Mg	mg/l	12,2	6,67	3,28	6,59	11,9	3,3	7,383333333	7,263333333
Na	mg/l	17,7	19,5	21,9	19,7	18	22,1	19,7	19,93333333
TOT P	µg/l	1180	207	373	112		80,5	586,6666667	96,25
Al	µg/l	53,1	63,1	80,8	54,9	20,5	68	65,66666667	47,8
As	µg/l	115	7,59	8,86	7,94	99,9	8,16	43,81666667	38,66666667
Ba	µg/l	328	253	359	252	264	327	313,3333333	281
Cd	µg/l	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05
Co	µg/l	1,74	7,64	3,61	7,95	0,879	2,81	4,33	3,879666667
Cr	µg/l	<0,5	2,35	2,13	2,01	<0,5	2,15	2,24	2,08
Cu	µg/l	18	11	100	3,24	3,07	13,6	43	6,636666667
Mn	µg/l	323	1690	559	1750	117	514	857,3333333	793,6666667
Ni	µg/l	11,9	77,8	84,6	79	7,24	75,3	58,1	53,84666667
Pb	µg/l	0,462	0,501	0,603	0,2	0,2	0,2	0,522	0,2
Zn	µg/l	5,36	12,7	6,72	2,77	2,08	2,52	8,26	2,456666667
MeHg	µg/l	0,0138	0,034	0,0653				0,0377	
TOT Solids	mg/l	511	1874	2384,5				1589,833333	
NPOC	mg/l	406	2498	18,82	390	2367	18,8	974,2733333	925,2666667

The measured concentrations of different substances after the second column.



2 column		**unfilt**			**filtr**			**unfilt**	**filtr**
		11 May	*26 May*	*10 June*	*11 May*	*26 May*	*10 June*	*Average value for all dates*	
TOT N	mg/l	564	342	3,988	368	311	4,311	303,3293333	227,7703333
Cl	mg/l	35	35	20				30	
Ca	mg/l	136	136	140		123	142	137,3333333	132,5
Fe	mg/l	0,531	0,805	5,27		0,571	4,9	2,202	2,7355
K	mg/l	42,3	29,3	21,2		26,6	21,2	30,93333333	23,9
Mg	mg/l	14,7	5,8	2,44		5,21	2,38	7,646666667	3,795
Na	mg/l	18,6	25,8	18,7		23,3	18,7	21,03333333	21
TOT P	µg/l	1810	167	463		151	51,6	813,3333333	101,3
Al	µg/l	45,9	13,7	15,5		11,1	15,5	25,03333333	13,3
As	µg/l	892	6,68	5,95		7,72	5,62	301,5433333	6,67
Ba	µg/l	379	120	157		124	148	218,6666667	136
Cd	µg/l	0,05	0,05	0,05		0,05	0,05	0,05	0,05
Co	µg/l	1,48	14,1	8,76		14,5	7,58	8,113333333	11,04
Cr	µg/l	0,5	1,13	0,522		0,5	0,5	0,826	0,5
Cu	µg/l	59	7,47	68,1		5,99	1,45	44,85666667	3,72
Mn	µg/l	22,8	999	1360		995	1320	793,9333333	1157,5
Ni	µg/l	12,4	70,3	47,1		69,9	49,1	43,26666667	59,5
Pb	µg/l	0,33	0,381	0,358		0,2	0,2	0,356333333	0,2
Zn	µg/l	18,6	16	6,12		2,15	2,57	13,57333333	2,36
MeHg	µg/l	0,0422	0,0184	0,0139				0,024833333	
TOT Solids	mg/L	277	872,5	886,5				678,6666667	
NPOC	mg/l	335	906	12,96	190	823	12,69	417,9866667	341,8966667

Appendix 5- The total removal performance of the GAC.

(%)	**Sand filter**		**First column**		**Second column**		**Whole system**	
Substance	*Unfiltered*	*Filtered*	*Unfiltered*	*Filtered*	*Unfiltered*	*Filtered*	*Unfiltered*	*Filtered*
TOT N	17.3	22.7	-4.41	-5.8	40.2	52.67	51	61.9
Cl$^-$	18.6		41		42.9		90	
Ca	-21.9	-22.7	43.1	43	42.5	40.7	67	65.6
Fe	14.7	17.5	65.1	36.8	-20.1	-106	60	-35
K	-8.5	-8.4	14.4	14.5	31.4	47.5	41.6	55.2
Mg	38.8	37.5	-27.4	-25.6	-3.6	47.8	-56.4	21.4
Na	-6	-6.2	-1.7	-2	-6.8	-5.4	-9.5	-8.81
TOT Hg	-46.5	19.1	65.6	61.1	21.1	-63.6	73.8	70.8
TOT P	-17.37	4.8	-3.2	30	-38.6	-5.2	-120.2	29.9
Al	1.4	1.5	84.1	87.1	61.9	72.2	95.3	97
As	-17.8	-29	-436.75	-307	-588	82.8	-3424	28
Ba	-40	-29.3	7	13	30.2	51.6	29.6	57.6
Cd	-120	20	61.8	n.d*	n.d	n.d	16.2	20
Co	-37.7	-41	71.75	73.1	-87.4	-184	41	13.8
Cr	-12.8	-19	88	87.4	63.1	76	96.2	97.2
Cu	-1288	-513	65.7	21	-4.3	43.9	-237	-172
Mn	78	89	-40	-43.6	7,4	-45.8	-41	-120
Ni	-118	-30	90	90.6	25.5	-10.5	87.3	89.6
Pb	76.8	-2.4	77.2	56.8	31.7	0	97.5	55.7
Zn	-91.8	-121	85.1	94.3	-64.3	3.9	65.7	91.1
MeHg	-34.4		77.4		34.1		85.2	
TOT Solids	-32.8		67.5		57.3		86.3	
NPOC	6	11.3	30	28	57.1	63	77.3	80.5

*n.d=not detected. *A negative number indicates an increase in concentration over the columns.*

Appendix 6- Former measurements in L1 including UCL95.

Date		**2006 april**	**2006 nov**	**2007 may**	**2007 oct**	**2008 may**	**2008 may**	**2008 sept**	**2009 may**	**2009 sept**	**2010 june**	**2010 oct**	**Average value**	**STDEVA**	**Standard error**	**UCL95**	**EQS/Effluent limit**	
Temperature	^oC	6,2	11,4	10,6	12,3	12,7			10	12,9			10,87142857	2,325019201	2,150284123	13,02171		
pH		9,6	7,8	7,2	7,7	8,6			8	8	7,6	7,8	8,033333333	0,696419414	0,535315349	8,568649		
Conductivity	mS/m	250	235	580	295	480			400	540	430	400	401,1111111	122,4943309	94,15747789	495,2686		
Alcalinity	mg HCO3	1100	810	930	1200	1100			910	2700	-	2400	1393,75	825,0370362	689,7482234	2083,498		
TOC	mg/l	3500	15	3100	820	3600			2100	14	70	350	1507,666667	1564,156802	1202,317351	2709,984	< 4	
COD_{Mn}	mg/l	1400	16,3	1000	410	1295			850	330	470	200	663,4777778	491,9179093	378,1215776	1041,599	< 4	
N - tot	mg/l	1000	590	830	390	880			640	850	660	440	697,7777778	206,988996	159,1058269	856,8836	<0,3	
N - NH_4	mg/l	200	230	480	27	420			480	650	310	430	358,5555556	186,168681	143,1019161	501,6575	_/0,5	
N - NO_3	mg/l	0,63	0,1	0,1	0,1	0,1			0,1	0,1	0,1	0,1	0,158888889	0,176666667	0,135798021	0,294687	50/20	
P - tot	mg/l	0,54	0,23	0,26	0,39	0,61			0,26	0,58	0,83	3,6	0,811111111	1,064664788	0,818373801	1,629485	< 0,0125	
O_2 (saturated oxygen)	mg/l (%)	0,1	0,1	0	0,1	0			0	0	0,1	0,1	0,066666667	0,05	20,9197764	20,98644	_/8	
Cl	mg/l	53	40	77	35	59			55	60	81	34	54,88888889	16,84817827	12,95065626	67,83955	100 /_	
SO_4	mg/l	42	20,0	110	27	26			1,6	1,4	14	1	27	34,11290079	26,22149676	53,2215	100/_	
Al	mg/l	0,37	0,27	0,43	140	0,41	0,39	0,36	0,24	0,22	0,95	0,59	13,11181818	42,08453821	28,27277747	41,3846	_ /0,5	
As	mg/l		0,0062	0,0130	0,0061	0,0130	0,0170	0,0170	0,0110	0,0100	0,0087	0,0084	0,01104	0,003945236	0,002822252	0,013862	<0,0004	
Ca	mg/l	830	320	51	280	890	620	330	380	200	710	220	439,1818182	278,0132436	186,7718384	625,9537	_/100	
Cd	µg/l	0,1	0,1	0,4	0,04	0,1	0,4	0,02	0,1	0,4	0,1	0,12	0,170909091	0,1500303	0,100791727	0,271701	<0,01	
Cr	mg/l	0,018	0,0087	0,017	0,0062	0,022	0,021	0,017	0,012	0,01	0,019	0,0097	0,0146	0,005435623	0,003651701	0,018252	<0,0003	
Cu	mg/l	0,005	0,0023	0,013	0,003	0,0021	0,0083	0,0043	0,003	0,004	0,014	0,0054	0,005854545	0,004161818	0,002795947	0,00865	<0,0005	
Fe	mg/l	4,2	2,9	0,47	3,9	7,9	4,3	0,46	2,2	0,88	37	3,8	6,182727273	10,4458586	7,017623292	13,20035	0,5	
Hg (unfiltered, total)	µg/l			0,221	0,8	6,3			1,2	0,36		0,21	1,515166667	2,375633003	2,493073941	4,008241	<0,1	
Hg (filtered, dissolved)	µg/l	0,1		0,1	0,1		0,24	0,1	0,1		0,1	0,1	0,1175	0,049497475	0,041380924	0,158881	<0,05	
Methyl-Hg	ng/l		340	208	66	140			120	90	66	30	132,5	100,0899595	83,67730022	216,1773	<10	
K	mg/l	<100	40	5,7	41	74	55	58	51	59	53	53	48,97	22,53427692	15,13873323	64,10873	_ / 12	
Mn	mg/l	0,14	0,33	0,024	0,93	0,078	0,07	0,013	0,15	0,16	2,7	1,5	0,554090909	0,849473067	0,570683771	1,124775	_ / 0,3	
Na	mg/l	<50	24	2,6	20	32	24	22	21	22	20	21	20,86	9,364536585	6,291181281	27,15118	100/_	
Ni	mg/l	0,44	0,26	0,055	0,24	0,71	0,53	0,48	0,4	0,39	0,37	0,24	0,374090909	0,174482351	0,117218839	0,49131	<0,0007	
Pb	µg/l	0,75	0,5	2	0,15	0,66	0,54	0,38	0,5	2	2	3,7	1,198181818	1,088786647	0,731456823	1,929639	<0,2	
Zn	mg/l	0,025	0,008	0,02	0,005	0,013	0,01	0,0097	0,0078	0,0200	0,016	0,028	0,014736364	0,007634955	0,005129233	0,019866	<0,005	