

Water Framework Directive and Mixing Zone Guidelines

Applied on a Smelter and Mine Scenario at two Boliden Sites

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Water Framework Directives and Mixing Zone Guidelines – Applied on a Smelter and Mine Scenario at two Boliden Sites

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ABSTRACT

The Water Framework Directive (WFD) aims to protect the aquatic environment and human health by reducing pollutants at the source. In order to achieve this, the concentration of priority substances should be lower than Environmental Quality Standards (EQS) values at the point sources. There are cases when the priority substance exceeds the EQS at the effluent discharge, however, they should be met at a distance close to the discharge point. The zones in the vicinity of discharge points where the priority substances exceed the relevant EQS values are called mixing zones.

Article 4 of Directive 2008/105/EC allows member states to designate mixing zones when the pollutant concentrations exceed the EQS values at effluent discharges. But mixing zones should not affect the compliance of the rest of the water body with EQS standards. Therefore, mixing zone design should meet some defined criteria. Moreover for ensuring that design criteria are met and for facilitating the mixing zone application, member states are provided with a Mixing Zone Guideline.

This project applies the Mixing Zone Guidelines at the Rönnskär Smelter located in the Northern Sweden with effluent discharges to the Baltic Sea. A second assessment of mixing zones is done in a mine area with discharge to Brubäcken stream. A “Tiered Approach” used in the guidelines is followed in assessment of mixing zones. The priority substances considered in the effluents are Hg, Cd, Ni and Pb. In the Rönnskär Smelter at Tier 2 determination of mixing zone length is done by the Discharge Test provided with Mixing Zone Guideline. CORMIX model is used for prediction of mixing in Tier 3.

In the mine area the concentration of metals at the measured points showed no exceedence of EQSs, therefore there was no need for the mixing zone design. In Rönnskär, for effluents where more than one priority substance exceeded the EQS values, the mixing zones determination is done separately for each metal. Mixing zone AA-EQS criteria were met for each substance within a predefined distance of 500 m from each of the discharge points. However, much more investigation is needed related to the use of total and dissolved metals concentrations, consideration of background concentration and other input data which are site specific. Further research is also needed for mixing zone assessment where the effluent discharges contain multiple priority substances.

We also concluded that climate effects, seasonal changes and other factors related to the receiving water characteristics need further investigation for a proper implementation of mixing zones for protection of aquatic and human life in Sweden.

Table of Contents

1. INTRODUCTION.....	8
1.1 The “combined approach” in the WFD (2000)	9
1.2 Concept of mixing zones.....	10
1.3 Mixing process.....	10
1.3.1 Passive and active mixing.....	10
1.3.2 Jet and plume discharge	11
1.3.3 “Near field “and “Far field” regions	12
1.4 Design regulations of mixing zones in EU & US	13
1.4.1 Concentration criteria in EU countries.....	13
1.4.2 Concentration criteria in US	13
1.4.3 Size criteria	14
1.4.4 Alternative criteria for toxic substances in the US	15
1.5 Mixing zone shape.....	16
1.6 Mixing zone models	17
2. AIM	18
3. STUDY SITE	18
3.1 Discharge locations and characteristics	19
3.2 Receiving water location and characteristics	22
4. MATERIALS AND METHODS	23
4.1 GENERAL MODELING PROCESS.....	24
4.1.1 TIER 0.....	24
4.1.2 Tier 1.....	25
4.1.3 Tier 2.....	26
4.2 Discharge Test Model	26
4.2.1 Theory behind Discharge Test ¹	27
4.2.2 Input Data	29
4.2.3 Outputs.....	32
4.3 TIER 3.....	32
4.4 CORMIX	32
4.4.1 Input data	33
4.4.2 Outputs.....	40
4.4.4. Sensitivity Analysis	41
4.5 Mixing zones overlapping.....	41
4.6 MIXING ZONE INVESTIGATION IN THE MINE AREA.....	43
4.6.1 Site description.....	43
4.6.2 Materials and methods	44

5. RESULTS.....	45
6.1 Tier 0 (statistical test results).....	45
6.2 Tier 1	45
6.3 Tier 2 Discharge Test.....	46
6.4 CORMIX RESULTS	49
6.4.1 Sensitivity Analysis	49
6.5 Mixing zones overlapping.....	61
6.6 Results for the mine area.....	63
7. DISCUSSION	64
8. CONCLUSION	66
9. REFERENCES.....	68
I. APENNDIX	77

1. INTRODUCTION

Major industries use water in their main processes. Consequently, discharge from industrial activities to surface waters, can increase concentrations of chemical substances in the water (Bellucci et al., 2010), (Huang et al., 2010). Chemical pollutants from continuous discharge points may have adverse effects on aquatic environment (Salmons, 1995), (Schmitt et al., 2005), (Baillieul & Blust, 1999), (Cailleaud et al., 2011) and human health (Berger et al., 2009). In order to prevent these harmful effects on both aquatic environment and human health, in 2000 came into force the EC Water Framework Directive (WFD, 2000/60/EC), as a part of the EU environmental legislation.

The implementation of the WFD has been a challenge for all the EU member countries (Achleitner et al., 2005). And it still remains an ambitious task, to achieve a "good water status" for "each river basin" in EU countries. This seems especially difficult to be reached for the priority substances and persistent organic pollutants due to their specific characteristics, adverse effects on aquatic life and high circulation in global scale to the different water bodies (Fuerhacker, 2009). Furthermore a common approach is required from all the member countries that have obvious legislative, economical and ecological variations between them.

The WFD implementation difficulties on the administrative level have been mentioned in Sweden (Hedelin, 2005; Hammer et al., 2011), Germany (Kaika, 2003; Moss, 2003) and all other countries. Variation between countries has been reflected in the changes that their water management structure has followed for the implementation of the WFD. Thus in France, Netherlands and Denmark based on individual domestic impacts the WFD implementation process have followed different paths (Lieberink et al., 2011).

Another important aspect relates to the investments that each country and their industries should do for the application and achievement of the WFD goals. The extra implementation costs of the WFD estimated by Dutch authorities were at 2,9 billion Euros and it was almost impossible to make cost-benefits analyses for this process (PBL, 2008). Additional costs also occur due to investments in new waste water treatment technologies required from industries to use the Best Available Techniques (BAT) (Schultmann et al., 2001).

Moreover article 9 (1) of the WFD (WFD, 2000/60/EC) claims that the recovery cost of water services must include economic analyses and should also be made in accordance with a "polluter pays" principle. However, it seems complicated to evaluate the value of water use and to make appropriate judgments for the water users and the related cost benefit relationship. When the private sector is analysed, not only should private economical profit be considered but also the role and the impact of their products on society and environment. Analysis of water use cost for agricultural irrigation, aquaculture industries, households, salmon angling and power generation,

have concluded that different valuation methods estimate different values for the economical cost of water (Moran & Dann, 2008). Further issues related to economical cost of WFD implementation were discussed in details from Kallis & Butler (2001). Despite uncertainties in management strategies of the WFD (Raadgever et al., 2011) related to diversity on economical, natural, technical and social systems of different countries, the WFD has started to be implemented in EU countries. Further information on how the WFD has already been applied in Sweden, Finland, Estonia, Denmark, UK and France were given at KSLA (2005) report. However, the implementation process brought up additional technical matters of discussion, one of which was application of combined approach (Achleitner et al 2005). This was set in article 10 of WFD (WFD, 2000/60/EC).

1.1 The “combined approach” in the WFD (2000)

The “combined approach” of the WFD (WFD, 2000/60/EC) states that control and prevention of pollution should be made using emission limit values (ELV) and environmental quality standards (EQS). ELV refers to the concentration of the pollutant that is permitted to be discharged from a specific installation to the environment in a given period of time (OEC 2007).

Therefore, ELV is a parameter measured at the end of the pipe while EQS as described in Article 2(35) (WFD, 2000/60/EC), determines the concentration of particular pollutant or a group of pollutants in water, sediment, or biota which should not be exceeded for protection of human health and environment. EQS gives a limitation for the concentration of a pollutant in receiving waters considering physical, chemical and biological responses towards the quantitative value of the discharge concentration (Jirka et al., 2004). But the main problem is that in the WFD there was not given adequate information where in the water body or how far away from the discharge point the EQS should be applied. Jirka et al., (2004) has analyzed two the following scenarios for applying the EQS in a water body:

- a) Applying the EQS immediately after the discharge point (at the end of the pipe), which mean that the EQS value will be more or less the same with ELV.
- b) Or application of the EQS after the complete mixing of discharge water with the receiving water body has occurred. In order for complete mixing to occur

between a discharge and receiving water large areas of the sea or river would have pollutant concentrations higher than EQS.

These two extreme scenarios raised the need of designing mixing zones aiming for a logical application of the “combined approach”. Thus a proper implementation of EQS to coastal and fresh waters required a clear mixing zone regulation for the point source discharge (Jirka, et al., 2004).

WFD 2008 adds the option of designing mixing zones for cases where the concentration of priority substances in the vicinity of discharges from point sources exceeds the relevant EQS.

1.2 Concept of mixing zones

Article 4 of the WFD allows for the application of mixing zones which can be designate adjacent to discharge points. Within the mixing zones the concentration of one or more of the priority substances listed in Part A of Annex I, may exceed the relevant EQS values. But the rest of the water body should be in the compliance with EQS standards and not be effected by mixing zones (WFD, 2008/105/EC).

Even if the private sectors use the BAT for the water treatments, the concentration of some pollutants can be exceeded at the discharge points. In order to insure the protection of surface waters the United States Environmental Protection Agency (USEPA) has allowed different States to make their own decision for the design of the mixing zones (Schnurbusch, 2000).

In the US, however, mixing zone application has a traditional use, for most of the EU countries this is a new concept. But for a better understanding of the mixing zone design and implementation basic technical information of the physical mixing process is needed.

1.3 Mixing process

Due to the characteristics of the effluent discharge and receiving waters, mixing process can be classified in different ways. The basic knowledge is given at the following sections.

1.3.1 Passive and active mixing

Passive mixing process occurs when the velocity of the effluent source is low and mixing is caused due to diffusion and advection that exist in the environment (Jirka, 2010).

Active mixing occurs when the source velocity is high and it cause the generation of the mean and random field velocity. This is caused by effluent momentum or buoyancy.

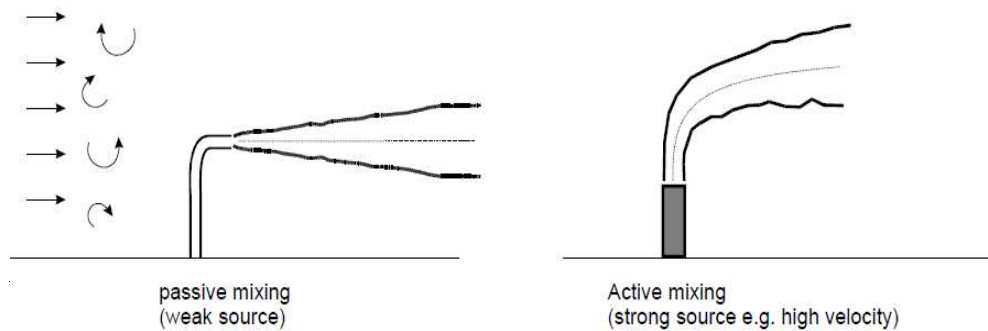


Figure 1. Passive and active mixing. From Jirka (2010)

Depending on the effluent and environment characteristics mixing can be passive, active or go through both processes. Discharge and receiving water characteristics play an important role in the way how the mixing occurs.

1.3.2 Jet and plume discharge

Related to the characteristics of the effluent and ambient conditions there are also two different terms used to define effluent discharge. Discharge in the mixing process can be defined as plume or jet.

The term jet is used when discharge velocity is high compared with the ambient conditions. The momentum effects are more important than density differences and buoyancy effects for the mixing. Thus the turbulent mixing is caused mainly by initial momentum flux of the source (Schnurbusch, 2000). When both the initial momentum flux and buoyancy plays an important role in the turbulent mixing (Fig.2) the discharge is called buoyant jet (Donker & Jirka, 2007).

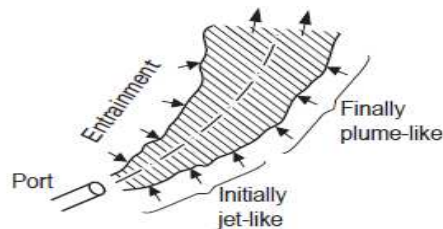


Figure 2. Buoyant Jet in the stagnant ambient. From Donker & Jirka, (2007).

Whereas when turbulent mixing is caused mainly by the density differences and initial momentum effects are not important the discharge is called plume (Fig. 3). The buoyancy flux plays the main role in the mixing process.

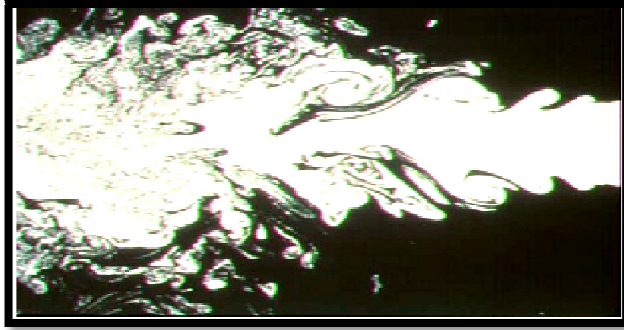


Figura 3. Scherlin photograph of a turbulent buoyant plume, showing the turbulence of mixing. (Photo: Schon, Univ. of Lyon). From Schnurbusch (2000).

Even when discharge is jet, as the distance of discharge from the source increases, the effects of momentum in the mixing process started to decrease. As a result the initial flow at the beginning is controlled by momentum and far away from the source by buoyancy. The discharge characteristics pass from jet to plume (Fig.2).

1.3.3 “Near field “and “Far field” regions

The mixing process can be also conceptualized as it occurs in two separate regions. The first region is “near field “and the next one “far field” region (Jirka et al., 2004). When the discharge starts to release to the ambient waters the first stage of mixing occurs in the “near field”. Mixing process and effluent trajectory are controlled by discharge characteristics such as initial jet momentum, buoyancy flux and outfall geometry (Jirka et al., 2004; Schnurbusch, 2000). In the “near field” initial mixing can be effected even by design characteristics of the outfall or diffusers.

As the distance of the discharge from the source increases, source characteristics become less important for the mixing process (Jirka et al., 2004). Existing ambient conditions start to control trajectory and dilution of the turbulent plume. Thus in the “far field” region, buoyant spreading motions and passive diffusion due to ambient conditions become the main processes that control mixing (Jirka et al., 1996).

Ambient conditions refer to dynamic and geometry characteristics of receiving water’s body (Donker & Jirka, 2007). The velocity and density of the receiving waters especially near the discharge point define the dynamic parameters of the

ambient. The geometry characteristics are related with depth, bathymetry (cross section) and plan shape of the water body especially in the vicinity of the discharge. Discharge conditions in mixing models are defined by discharge flux and discharge geometric characteristics. Effluent flow rate, momentum flux and buoyancy are used to describe discharge flux characteristics (Jirka et al., 1996).

The discharge geometric characteristics for submerged single port discharge are defined by the port diameter, the outfall orientation and its elevation from the bottom of the water body. For the surface discharges the geometry of the port and the orientation of the discharge towards the receiving waters are the main geometric parameters that can be considered (Donker & Jirka, 2007).

1.4 Design regulations of mixing zones in EU & US

Regulation of the mixing zone design is based on two main parameters. These are the maximum concentration of substances that can be exceeded within the mixing zone and maximum allowable size of the zone (Ragas et al., 2005).

1.4.1 Concentration criteria in EU countries

In the EU countries the mixing zone can be applied based on the annual average criteria (AA-EQS) and/ or maximum allowable concentration (MAC-EQS) of the priority substances (EU-EQSD, 2010,a). Annual average criteria are related with the chronic effect of hazardous substances on aquatic environment and human health. Whereas the maximum allowable concentration refers to the acute affects in a short-term exposure. For some of substances such as lead or nickel only annual average criteria are applied since these values are considered to be safe even for the short-time exposure (WFD, 2008/105/EC). For the other substances listed in the Part A of Annex I, both criteria should be met.

In the Netherlands a single value called Maximum Permissible Concentration (MPC) is used as zinc (Zn) and copper (Cu) concentration criteria. Due to the Dutch Environmental Quality Standard the discharge is not allowed to contribute more than $0.1 \cdot \text{MPC}$ at the end of the mixing zone or the increase on concentration of relevant substances at the end of the mixing zones should not exceed 10% of the local background concentration (RIVM,2008).

1.4.2 Concentration criteria in US

Similar to the EU (EU-EQSD, 2010, a) the US EPA maintains two water quality criteria for toxic substance concentrations but there are two types of mixing zones.

The first zone is acute mixing zone (US EPA, 1991) or zone of initial dilution (ZID) (Schnurbusch, 2000), which is the area immediately after the discharge surrounding the outfall (Fig.3). Inside this zone the Criteria Maximum Concentration (CMC) applied for the acute toxicity can be exceeded but should be met at the edge of the zone (Schnurbusch, 2000).

The next area, the formal mixing zone is defined as chronic mixing zone (US EPA, 1991). In the formal mixing zone, acute criteria should be met, but Criteria Continuous Concentration (CCC), applied for chronic toxicity, can be exceeded. Chronic criteria should be met outside mixing zones.

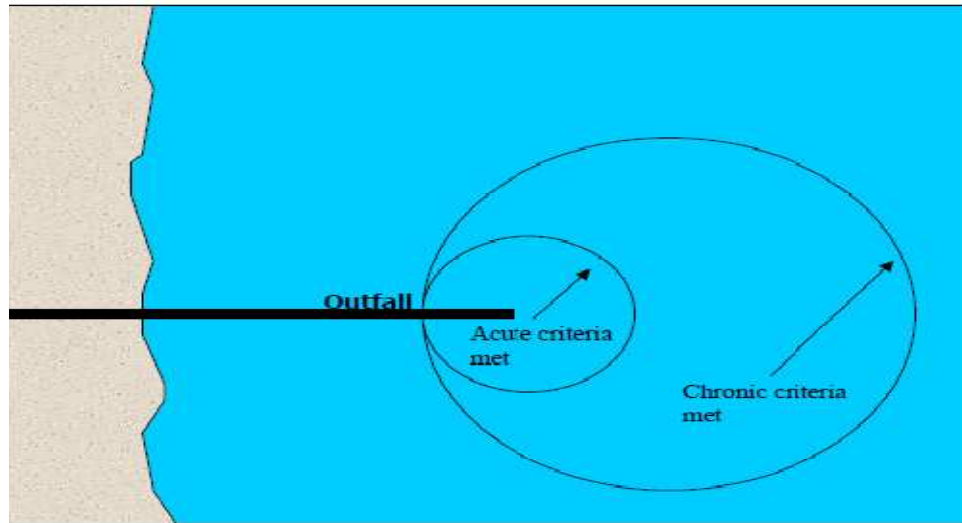


Figure 4. Mixing zone design based on acute and chronic concentration criteria in US. From Schnurbusch (2000)

The CMC is almost equivalent with Maximum Admissible Concentration (MAC) applied at EU WFD (EU EQSD, 2010, b). Moreover in both cases the restriction is used to prevent the adverse effects such as acute toxicity to the aquatic organism passing through the mixing zones. Therefore, based on the concentration criteria the mixing zone is considered as an area where the water quality criteria can be exceeded as long as acute toxic condition are prevented (US EPA, 1991)

1.4.3 Size criteria

Mixing zone design should be made in such a way to ensure that not only the aquatic life but also the whole integrity of water body is protected. Thus, the second determinative factors considered in the design are dimensions of mixing zones.

A tier approach is followed in the mixing zone guidelines document set for EQS under the Water Framework Directive (WFD, 2008/105/EC). In the second tier for rivers if the EQS are not exceeded within a distance of $10 * W$ (river width) or 1000 m which does not exceed $0.1 * L$ (river length) no further assessment is needed.

A similar approach is used for chemical substance in Netherlands and Austria where the mixing zone length (L) should be $10 * W$ (width of water body) and maximum 1 kilometer (EU EQSD, 2010, b).

In order to protect the migratory species that pass through the mixing zone in some countries the mixing zone criterion is related also with width of water body. For cooling waters in canals, tidal harbors and rivers in the Netherlands a mixing zone is allowed to be extended in the maximum 25% of wetted cross-section of the water body (Baptist & Uijttewaal, 2005).

But for large waters bodies such as lakes and seas, the width of the water body is not a limiting factor. Therefore, the length of mixing zones for lakes in Netherlands is calculated to be proportional to area, length and the width of the water body using the following equation

$$L_{\text{mixing}} = \sqrt{\frac{A}{\frac{L}{B}}} / 4 \quad \text{Equation 1}$$

where the L_{mixing} is the length of mixing zone, L is length of lake, B width and A is lake area (EU EQSD, 2010, b).

Hence, for very large water bodies a maximum 1000 m length and 100 m width is set as a limitation for the size of mixing zone.

Even the default length of mixing zones used in the discharge test of EU Guideline for EQS is calculated due to the dimensions of the water bodies. For rivers, canal, ditch and small canals based on EQS values length of mixing zones is estimated as L_{min} ($10 * \text{width of water body}$ but with max value 100 m) and for MAC criteria as L_{min} ($0,25 * \text{width of the water body}$ with max value 25 m) (EU EQSD, 2010 c).

1.4.4 Alternative criteria for toxic substances in the US

In US four alternative ways are provided to prevent the effect of acute toxicity for organisms passing through the mixing zone area (Jirka, 1992). These include:

- The “criterion maximum concentration” (CMC), should be met within the pipe
- The CMC can be met within a short distance from the discharge point. But in order to achieve a rapid mixing and minimize the exposure time of organism to toxic substances the discharge velocity should be 3m/s.

- It should be shown that a drifting organism it's exposed no longer than 1 hour to average concentrations which exceeds the CMC.
- The last alternative is related to the geometric restriction for zone of initial dilution (ZID). In order to met CMC criterion, one of the follows limitation should be applied
 1. Within 10% of the distance starting from the edge of outfall structure, ending at the edge of regulatory mixing zone, the CMC should be met. These criteria must be applied for any spatial direction.
 2. In any spatial direction the CMC should be met within a distance which is $50 \cdot \sqrt{\text{cross section area of discharge outlet}}$. This criterion aims to ensure a minimum dilution factor of 10 within the required distance.
 3. In any horizontal direction, the CMC should be met within the distance 5 times the water local depth.

1.5 Mixing zone shape

In the EU guideline of mixing zone annexes (EU EQSD, 2010,b), in the simple assessment of Tier 2, for lakes the mixing zone shape is allowed to be a half circle. Within the same Tier the shape of mixing zone for the discharge shoreline to the sea is also considered to be a half circle with a diameter equal to mixing zone length (L_{mixing}). Therefore the mixing zone is located in the distance $L/2$ mixing upstream and $L/2$ mixing downstream of the discharge. For a mixing zone with maximum length of 1000 m, the shape is a half circle with a radius of 500 m. In Netherlands the mixing zone in shoreline and open sea is determinate as a maximum volume of a half circle with an assumed average depth (EU EQSD, 2010,b).

For coastal waters, lakes and estuaries in the US, the surface area limitation for the mixing zone includes benthic area and underlying water column (Jirka et al., 1996). US EPA requires that mixing zone shape must be indentified in an easy way (Schnurbusch, 2000).

Hence the mixing zones of discharges to lakes and coastal waters from municipalities and industrial, US EPA uses the term zone of initial dilution (ZID). Due to US EPA (1982) requirements, a (ZID) should be a regularly shaped area such as circular or rectangular that surrounds the discharge structure with a design that should encompass the region where the standards are exceeded (Jirka et al., 1996). Other factors considered in the design of mixing zones are size and character of the receiving waters. In mixing zone implementation guidance for streams, depth, width

and shape of the stream channel are considered because they affect the mixing process (CDPHE, 2002).

Therefore the shape and size of mixing zones can vary due to the size of receiving waters, their location, character and use (FWPCA, 1968).

When there is no specific dimension available for application of mixing zones, the size and shape is determined case by case (Jirka et al., 1996).

1.6 Mixing zone models

Mixing zone design is based on the use of different models and more than one model may be necessary to adequately describe the behavior of discharges.

CORMIX and PLUME are the most common models used for mixing zone development in the US. Hydraulic models developed in Europe include DHI Software models (Denmark), Delf Hydraulic Software (Netherlands) and TELEMAR-2D (Germany). Information for these models can be found even at Mixing Zones Guidelines documents.

CORMIX

The Cornell Mixing Zone Expert System (CORMIX) is a series of software for the analysis and design of mixing zones for discharges that contain conventional and toxic pollutants. CORMIX 1 is used for single port negatively buoyant and non - buoyant discharges, into stratified or unstratified river, lake or coastal water in stagnant conditions (Doneker & Jirka, 1990); CORMIX 2 is used for multiport diffusers (Akar & Jirka, 1991); CORMIX 3 is used for buoyant surface discharges where an effluent enters laterally to a large water body (Jirka et al., 1996). DHYDRO (available in current CORMIX versions) analysis dense or sediment discharges in coastal waters (Doneker & Jirka, 2007).

PLUME

The Visual Plumes (VP) model system predicts dispersion and other physical processes that affect surface waters (Frick, 2004). It simulates jets and plumes discharge waters. VP is used to simulate single submerged plumes in stratified waters and for supporting far field and multiple dilution models (Frick et al., 2002).

DHI Software models

Danish Hydraulic Institute MIKE Software models are used for hydrodynamic modeling of streams, lakes (Dupont, 2010), sewage, industrial discharges, drinking and coastal waters (Gierlevsen et al., 2001). They are also applied in watershed modeling and for prediction of pollutant trends in the rivers (Vaitiekūnienė & Hansen, 2005)

DELFT Hydraulic Software

Delft3D, are 2D/3D modeling system, developed by Delft Hydraulics (www.wldelft.nl), to investigate the water quality, sediment transport, river morphology, coast waters and estuaries (Hsu et al., 2006).

TELEMAC

The TELEMAC is a software system designed to provide information for different physical process in water. TELEMAC-2D is used for tidal currents (Giardino & Monbaliu, 2005).

DISCHARGE TEST

The Discharge Test software is a simple macro based MS Excel model given as a part of EU mixing zone technical guideline. This program is provided for EU member states to be used at the Tier 2 level of assessment for discharges to the fresh surface waters. The Discharge Test is a simple tool for mixing zone design used before applying more complicated hydraulic models.

In this study, the Discharge Test program is used for mixing zone design in Tier 2 and CORMIX systems in Tier 3.

2. AIM

The aim of this project is to determine the applicability of WFD mixing zone guidelines for the Rönnskär Smelter and mine facilities with effluent discharges to the Baltic Sea and Brubäcken creek.

Another objective of the study is as follows

- Through the application of the mixing zone design process, find recommendation for improvement of current mixing zone guidelines

3. STUDY SITE

The Rönnskär Smelter in Skelleftehamn, Northern Sweden (64°40'1"N, 21°16'11"E) is one of the biggest Cu smelters in the world. The smelter is located near Skellefteå on the west coast of the Gulf of Bothnia (Fig.5) in a small peninsula (Beckam, 1978).

The main metals produced from Rönnskär smelter are copper (Cu), lead (Pb), zinc (Zn) clinker, gold (Au) and silver (Ag). 75% of the metals used in the smelter processes come from mine concentrates and 25% from recycling materials. Consequently the effluent discharges which come from industrial processes contain Cu, Pb, Zn, cadmium (Cd), arsenic (As), mercury (Hg) and nickel (Ni).

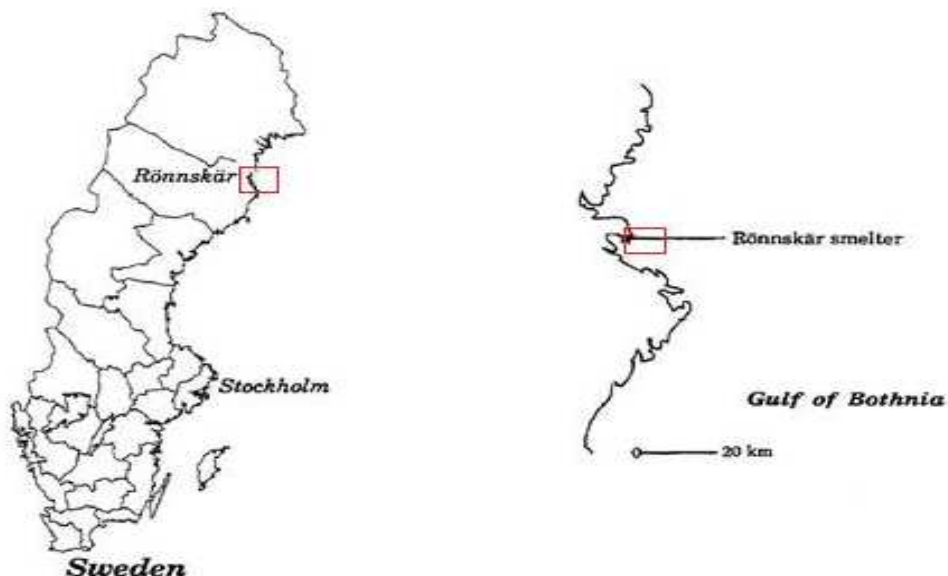


Figure 5. Location of Rönnskär Smelter in Northern Sweden. Modified from Johnson., et al (1992)

3.1 Discharge locations and characteristics

Around Rönnskär Smelter are located 7 effluent outlets points (Fig.6) with discharge to the Baltic Sea. All effluent discharges receive water from different processes. Therefore the metal concentrations and water temperatures are specific in each case.

An exception to this are discharge points 1 (Avlopp 1 östra and Avlopp 1 västra) and 3 (Avlopp 3 and Avlopp 3 västra) where discharge water comes from two different locations: point 1 east and 1 west and point 3 east and 3 west. After mixing, the water is discharged from each location to the sea through one single outlet (outlet 1 and outlet 3, Fig 6). In addition to the variability in effluent characteristics, the discharge points differ in outlet shape, size and location related to the water surface. The main characteristics of the discharge locations for this project are given in Table 1.

Table 1. Location of discharge pipes and main characteristics of effluent discharge points in the Rönnskär Smelter

Discharge points	Discharge coordinates (in grad, minute, seconds)	Location of pipes from the surface water	Pipe inner diameter (m)	Effluent temperature (°C)
Point 1	N 64° 39,762' E 21° 16,288'	At the level of the sea surface	1	25-30
Point 2**	N 64° 39,900' E 21° 17,082'	A little above the sea surface	0.6	25
Point 3	N 64° 39,900' E 21° 17,082'	At the level of the sea surface	1	25
Point 4	N 64° 40,198' E 21° 16,768'	2 m depth below the sea surface	0.8	15-25
Point 4 West	N 64° 40,257' E 21° 16,454'	0.5 m depth below the sea surface	0.8	15-25
Granulation water*	N 64° 40,283' E 21° 16,137'	At the level of the sea surface	1*	40
Sanitary water	N 64° 40,497' E 21° 15,093'	2 m depth below water surface	0.2	18

Note: *The granulation water is discharges to the sea surface through a ditch. Pipe diameter is an approximation.

**Outlet pipe at point 2 was located above the sea surface but is considered at the sea surface.

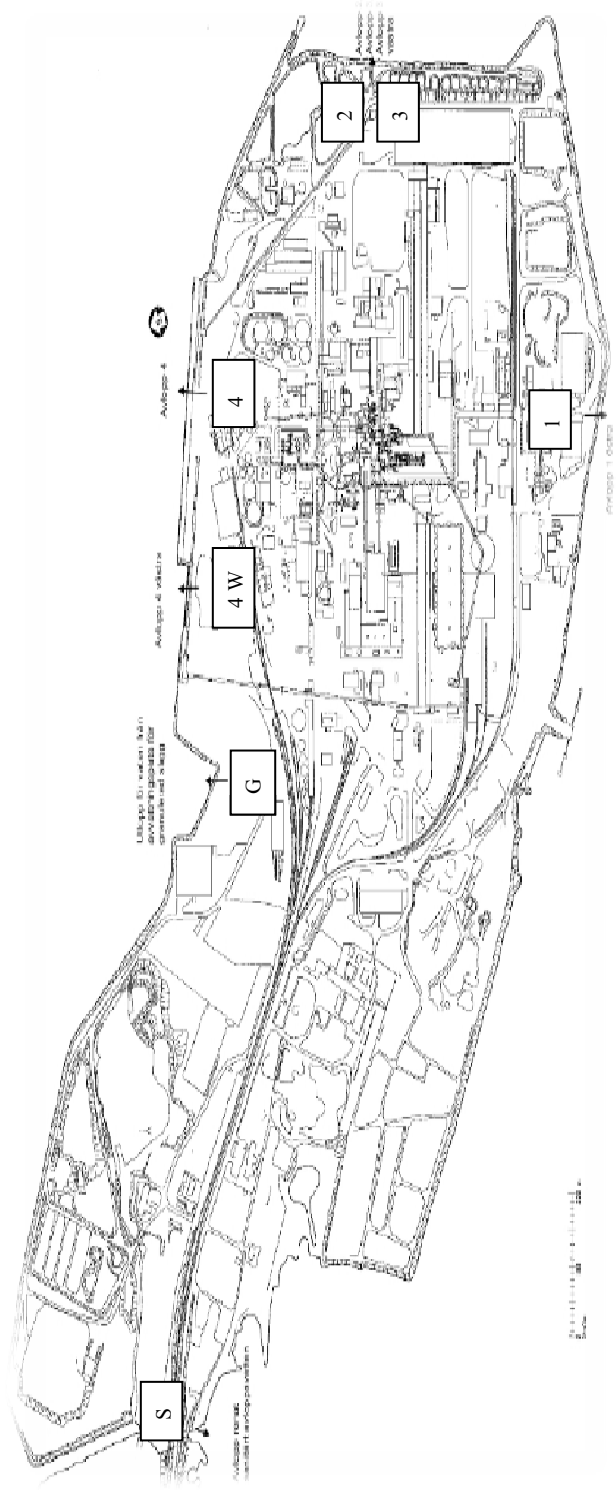


Figure 6. Map of Rönnskär Smelter discharges to the Baltic Sea. In the counter-clockwise direction there are shown discharge point 1 (Avlopp 1 östra and Avlopp 1 västra), discharge point 2 (Avlopp 2), discharge point 3 (Avlopp 3 and Avlopp 3 västra), discharge point 4 (Avlopp 4), discharge point 4 west (4W) (Avlopp 4 västra), discharge of granulation water (G) (Uttlop för vatten från avvattningsplats för granulerad slagg) and discharge of Sanitary water (S) (Avlopp renat sanitärt avloppsvatten). From Boliden AB

3.2 Receiving water location and characteristics

Location and dimensions. The Gulf of Bothnia is the northernmost part of Baltic Sea located between Sweden and Finland (Fig.7). Considered as an estuary the Gulf of Bothnia can be divided in two main basins (Omstedt, 1983) which are the Bothnian Sea between latitudes (60.5°N and 63.5°N) and the Bothnian Bay between (63.5°N and 66°N) latitudes (Håkansson et al., 1996). The Bothnian Bay is a semi-enclosed area (Fig.7), from Kemi (north) to Umeå (south)(Nohr, 2005). The dimensions of Gulf of Bothnia and Bothnian Bay are given as follows

Table 2. Dimensions of Gulf of Bothnia and Bothnian Bay

Receiving waters	Length (m)	Width (m)	Depth (m)	Basin area km ²	Volume km ³
Gulf of Bothnia	725 000	80 000- 240000	60	102 000	5 830
Bothnia Bay	315 000	180 000	43	36 800	1 490



Figure 7. View of Gulf of Bothnia and Bothnian Bay with location of Rönnskär Smelter.

Salinity and temperature. Gulf of Bothnia has brackish water with a lot of rivers discharging to the coastal areas. Therefore the surface water salinity in the Bothnian Bay

shows seasonal variations. Taking into account even seasonal effect, the salinity in the coastal surface of bay can be considered between 2-4 practical salinity units (psu) (Granskog M.A et al., 2005).

The average temperature and salinity data from 1970-1995 observed in three stations, from the water surface until 200 m depth are given by Håkansson et al., (1996). In this study a mean value for temperature and salinity is considered for all receiving waters.

Currents and wind speed. The main movement of water in the Gulf of Bothnia and Bothnia Bay are due to water currents and wind speed. The currents velocities in the open sea at 2-5-7.5 m layer are 1-2 cm/s and near the coast 4 - 6 cm/s (Myrberg & Andrejev, 2006).

In Gulf of Bothnia the mean daily wind speed for 2002 reported from 10 stations at the lower range was 5 m/s (Algesten et al, 2006). A fixed wind that changes direction from east to west with a speed of 5 m/s for the same area is used in the model by Nohr (2005). Boliden has also measured wind speed around Rönnskär in the 6 sample points for 2007, 2008, 2009 and 2010 from May to November and an average 4.8-5.5 m/s velocity was obtained from the registered data. Therefore an average wind speed used in this project was 5m/s.

Background metals concentration. Total metal concentrations in the coastal waters of Gulf of Bothnia and Bothnian Bay were assumed to be similar to concentrations in the Bothnian Sea (Herbert et al., 2009, Table 3).

Table 3. Background concentration of Cd, Pb, Hg and Ni metals in (µg/l) in the Bothnian Sea.

Metals	Cd	Pb	Hg	Ni
Background concentration (µg/l)	0.023	0.067	0.0038	0.839

4. MATERIALS AND METHODS

This project is developed based on a tiered approach within the Mixing Zone Guidelines Document (EU EQSD, 2010, a). The method aims to identify discharges which are not a matter of concern related to EQS in each tier, highlights discharges that need further investigation, and the continues to the next tier (EU EQSD,2010a). This investigation continues with mixing zone identification, design and further complex assessment at the Tier 3. A simple schematization of tiered approach is given in Fig.8.

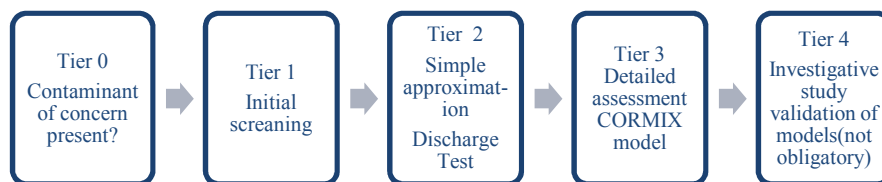


Figure 8. Schematization of “Tiered Approach”. Modified from (EU EQSD, 2010a).

4.1 GENERAL MODELING PROCESS

Detailed information for application of Tiered Approach, explanation of Discharge Test and CORMIX models are given at the following sections.

4.1.1 TIER 0

At the first step of Tier 0, the presence of Cd, Pb, Hg and Ni in the discharge water were determined for each of the 7 outlets. These are the metals included in the list of priority substances in the Annex I of the WFD (WFD 2008/105/EC).

The second step was related to the concentration of metals found at water discharged from each point. The aim was identification of discharge points where metals concentrations exceeded parameters set for Environmental Quality Standards (EQS). These parameters included AA-EQS and MAC-EQS. EQS values refer to the dissolved fraction of metals in water samples obtained by sample filtration through a 0.45µm filter or similar pre-treatments (WFD 2008/105/EC). Generally companies report metal concentrations as total (dissolved plus particulate) values. Therefore in the mixing zone Annexes 7.1 is clarified that effluent total metals concentrations in Tiers 1 and 2 can be treated as dissolved.

Thus in this stage total metal concentrations were assumed to have 100% partitioning in the dissolved phase for all discharge points. This was done until the application of the CORMIX model (discussed later).

The metals data used at this stage were monthly total metal concentration (µg/l) at each discharge point measured during 3 years 2008-2010. An annual average metal concentration was determined at each discharge point for each year. The reported data were given for 12 or 11 months of the year and for granulation water only for 6 months. It should be noted that an arithmetical average of available data (for sites without year-round data) was as assumed to be representative of annual average data.

In some cases, values were lower than the detection limit and thus the detection limit was used. This was considered a conservative approach for toxicity and environmental criteria.

For discharge points 1 and 3, where discharge water comes from two different pipes (1 east, west and 3 east and west), mixes, and discharge at a single outlet, average concentration was calculated according to:

$$C_{\text{tot}} = \frac{F_1 C_1 + F_2 C_2}{F_1 + F_2} \quad \text{Equation 2}$$

where C_{tot} is the metal concentration at the final outlet, F_1 is the flow from one outlet and F_2 is flow from the other outlet. C_1 and C_2 are concentrations at effluents F_1 and F_2 . Average yearly concentrations for all discharge points of Cd, Hg, Pb and Ni were compared with their respective AA-EQS values (Table 4). For Cd and Hg, which have also MAC-EQS values set, the maximum concentration values were compared with respectively MAC-EQS values. This was done only for the data of 2010. For Cd the MAC-EQS values depend on water hardness and we used a conservative case for water hardness of class 1 where CaCO_3 concentration is $< 40\text{mg/l}$ and MAC-EQS is $0.45(\mu\text{g/l})$

Table 4. AA-EQS and MAC-EQS values for Cd, Pb, Hg, Ni, included in the priority substances list.

Metals	Cd	Pb	Hg	Ni
AA-EQS ($\mu\text{g/l}$)	0.2	7.2	0.05	20
MAC-EQS ($\mu\text{g/l}$)	0.45 (Class 1)	-	0.07	-

For the metals concentration that exceeded the AA-EQS values, a one tailed t-test was used to determine which concentrations exceeded standards at least 90% of the time during 1 year. In cases where the AA- EQS was exceeded, the investigation moved to the next level (Tier 1).

4.1.2 Tier 1

Tier 1 is a simple assessment to determine if analysis of a discharge concentration, after initial mixing with the receiving water, should move to the next stage (i.e. it still does not meet the standard). This is a simple way to determinate how significant the added discharge of a pollutant is for the receiving water body. At this tier, the assessment for fresh water and coastal waters differ due to the specific properties of rivers, lakes and coastal waters which can affect the mixing process. The first stage of coastal waters test was applied. (EU EQSD, 2010, a). For this the locations of all the discharge points were checked and analyzed related to sea surface (Table 1), in order to see if the discharge was covered all the times by water. For the discharges near to the surface and not well covered all the times by water the risk of running undiluted across the foreshore was considered high. The dilution rate in this case could be low

resulting in a large area where the EQS can be exceeded. For coastal waters as in these cases where there is place for uncertainties is recommended to proceed to next Tier. Thus discharges analysis proceeded to Tier 2 for the 7 discharge points at Rönnskär.

4.1.3 Tier 2

Tier 2 is the first step in estimation of the exceedence of EQS in the receiving water bodies starting from the discharge point. The calculation of dilution of discharge as a function of distance from the discharge points and extent of EQS in the receiving water was made using Discharge Test model.

4.2 Discharge Test Model

An overview of the Discharge Test model is shown in table 5 and a general illustration of the model is given at Fig.9.

Table 5. Explanation of worksheets of the Discharge Test. Modified from Discharge Test User Manual

Worksheet	Purpose/function
1)Discharge-test	In this worksheet the inputs of ambient, discharge, quality data and the general results of the assessment are presented
2)Calculation of mixing	In this worksheet calculations are carried out and detailed information concerning the dimensions of the mixing zones and consequences at a water body level presented
3)Standards	A list of substances and related EQ standards
4)Legend	A short summary of the parameters used
5)Mixing in tidal waters	In this worksheet the calculations for tidal waters are carried out based on input for the AA-EQS-assessment and the MAC-assessment.

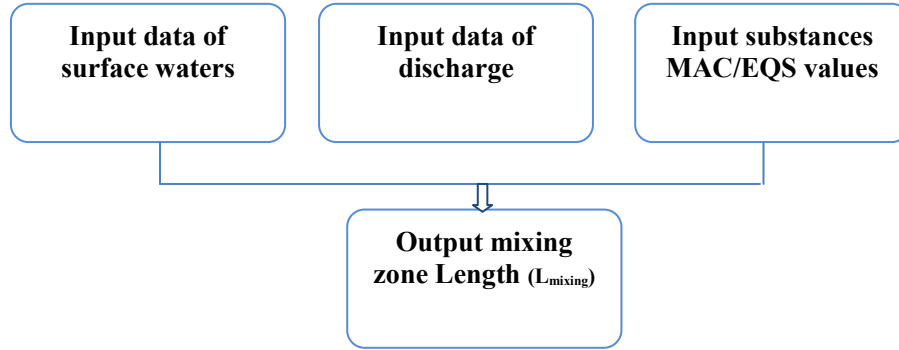


Figure 9. Illustration of Discharge Test model used at Tier 2 of Mixing Zone assessment.

4.2.1 Theory behind Discharge Test¹

The Discharge Test model is used to calculate the dimensions of the mixing zone. Therefore in a rough way it calculates the mixing of discharge with receiving waters and dilution from the discharge point until a default distance. The dilution as a function of the distance is estimated based on the Fischer equations (3-8).

$$\varphi(x,y) = \frac{W}{a \cdot u \cdot \sqrt{\pi \cdot K_y \cdot \frac{x}{u}}} \cdot \sum_{n=-\infty}^{n=\infty} \exp \left[-\frac{(y-2 \cdot n \cdot B)^2}{4 \cdot K_y \cdot \frac{x}{u}} \right] \quad \text{Equation 3}$$

$\varphi(x,y)$ is the concentration of investigated substances from the discharge point at a distance x in horizontal direction and distance y from the river or other receiving surface waters bank. x is the distance to the point of discharge (m), with a maximum value (L), W is load of emitted substance (g/s), a is the depth of receiving waters (m), B is width of receiving waters (m), u is flow rate of receiving water (m/s), n is the number of the imaginary sources (Socolofsky, 2005) or situations that contribute to the concentration, and K_y stands for the transversal dispersion coefficient in y direction. K_y is calculated as follows:

$$K_y = \max(\alpha \cdot u \cdot a \sqrt{10/C_{chezy}} ; 0.001) \quad \text{Equation 4}$$

where α coefficient is 0.6, C_{chezy} is the Chezy constant calculated in equation 5,

¹ Theory of Discharge Test is taken from Mixing Zone Guidelines documents

$$C_{chezy} = 18 \cdot \log \left(\frac{12 \cdot B \cdot a}{\frac{B+2a}{k}} \right) \quad \text{Equation 5}$$

where k is a bottom roughness constant (values change from 0.05 for rivers to 0.1 for canals or lakes)

At a distance of $x \leq L$ from the discharge point and where $y = 0$ (e.g. at a river bank) and for $n = 0$ the equation 3 can be written as follows

$$\varphi(L, 0) = \frac{W}{a \cdot u \cdot \sqrt{\pi \cdot K_y \cdot \frac{L}{u}}} \quad \text{Equation 6}$$

At a discharge point ($x = 0$) where the concentration of emitted substances is φ_0 and effluent flow rate is Q , the load of the emitted substances can be expressed as $W = Q \cdot \varphi_0$. Therefore, equation 6 can be written as:

$$\varphi(x, 0) = \frac{Q \cdot \varphi_0}{a \cdot \sqrt{\pi \cdot K_y \cdot u \cdot x}} \quad \text{Equation 7}$$

The dilution of discharge in the receiving waters is given by a dilution factor (M_x) calculated as $\varphi_0 / \varphi(x, 0)$.

$$M_x^{2D-Plume} = \frac{\varphi_0}{\varphi(x,0)} = \frac{a \cdot \sqrt{\pi \cdot K_y \cdot u \cdot x}}{Q} \quad \text{Equation 8}$$

These equations were taken as a base and developed further in the “Discharge Test” model. The dilution factor calculations were carried out separately for plume and jet discharges. The formulas used in each case are given at legend page of Discharge Test. At a distance L from the discharge points the increase in concentration of the substance of concern is estimated as $\Delta C_L = C_{effluent} / M_x^{2D-Plume}$. Fig. 10 shows mixing and dilution results based on the different formulas used.

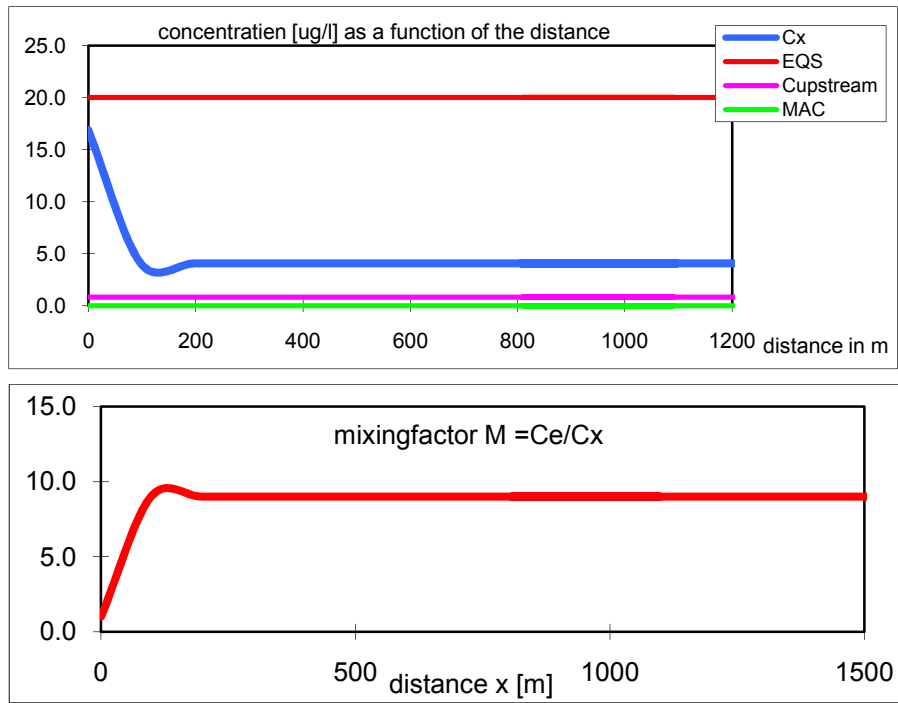


Figure 10. Mixing factor and dilution of effluent concentration as a function of distance demonstrated at the “Discharge Test” in one the project points.

The default value for acceptability of the mixing zone is estimated differently for rivers and lakes. For the rivers the mixing zone length should be lesser of 10* width of the water body where total length should not exceed 1 km. For lakes (used to determine mixing zones in this study) the default value is calculated based on the width and length of the water body. From these two dimensions a diameter of the lake is estimated from which the default length of the mixing zone is derived. Mixing zone length for lakes should be less than $\frac{1}{4}$ of the estimated diameter or where the water body is large the value should not exceed 1 km. This calculated mixing zone length is considered acceptable unless the discharge is located in a sensitive area. If the dilution is enough to meet the EQS values within these boundaries, the mixing zone can be recorded and the investigation should not continue to the further tiers.

4.2.2 Input Data

The “Discharge Test” was originally designate for the fresh waters. Four options for fresh waters (river, canal, ditch and small canal or lake) are available in the model. Thus, we are forced to treat the Gulf of Bothnia and Bothnian Bay as large lakes and run Discharge Test for these two sites

Input data of surface water:

Average ambient flow rate Q_{opp} (m^3/s) (Equation 9) was calculated for a rectangular area (A) near the discharge point, with a depth of 3 m and a length of 8 m. At this stage the water movement was assumed to be caused only from currents. Average current speed was 0.05 m/s.

$$Q = A \cdot V$$

Equation 9

Therefore in all cases the Q_{opp} was set $1.2 m^3/s$.

Dimensions of water body. The depth of 60 m, average width 160 000 m and length of 725 000 m were set for Gulf of Bothnia. For the Bothnian Bay dimensions used were depth 43 m, width 160 000 m and length 315 000 m.

Upstream concentration (CW). Background concentrations were used for upstream concentrations (Table 3). In order to see how much the background concentrations could affect the mixing zone dimensions, two assumptions with the background concentrations were made. At the first approximation we assumed that no (or very low) metal background concentration ($0.0001 \mu/l$) exists in the receiving water. The second case assumed background concentrations for trace metals (Herbert 2009) represented upstream concentrations.

Input data of effluent discharge:

Discharge Flow rate Q (m^3/hr). The yearly average volumetric discharge flow for years 2008, 2009, 2010 of each of the discharge point (Table 6) was used at this part.

Diameter pipe D (m) was the data of the inner diameter of the 7 discharge outlets displayed at Table 1.

Effluent concentration C_e (μ/l) was the average total concentration for Cd, Pb, Hg and Ni, discharged during one year displayed at Table 6. The Discharge Test bases calculations on total pollutant concentration, thus the assessment continued with the same concentration data used at previous Tiers.

From the list of substances available in the first sheet of Discharge Test were chosen the investigated metals. Related EQS and MAC-EQS values are then automatically determined by the model. Because EQS values were different for Cd, in coastal waters, an EQS value of $0.2 \mu g/l$ and a MAC-EQS value (soft water) of $0.45 \mu g/l$ were set manually.

Table 6. Annual average flow and total metal concentrations at each discharge point

Discharge Outlets	Year	Average flow (m ³ /h)	Pb (μ/l)	Cd (μ/l)	Hg (μ/l)	Ni (μ/l)
Point 1	2008	567	-	0.73	0.07	-
	2009	526	-	0.6	-	-
	2010	495	11.5	0.74	-	-
Point 2	2008	299.6	-	0.62	-	-
	2009	320.8	-	0.48	-	-
	2010	321.5	-	0.55	-	-
Point 3	2008	1566	-	2.02	1.09	-
	2009	1662	-	0.47	0.9	-
	2010	1429	-	0.7	1.13	-
Point 4	2008	3672	-	1.12	0.08	-
	2009	3492	-	0.88	-	-
	2010	4032	-	0.91	-	-
Point 4 West	2008	144	-	0.82	-	-
	2009	180	-	0.47	0.21	-
	2010	144	-	0.78	0.2	-
Granulation water	2008	406	41.64	0.41	-	31.67
	2009	346	71.85	0.34	-	33.57
	2010	405	71.34	0.20	-	33.34
Sanitary water	2008	4.32	162.58	7.35	0.5	37.5
	2009	4.32	108.83	3.93	0.38	25.5
	2010	5.04	119.36	7.85	0.23	437.55

4.2.3 Outputs

After the determination of the mixing character (plume or jet), the mixing factor (M_x) was calculated as a function of the distance in each case. Mixing zone length was then estimated and bounded by AA-EQS or MAC-EQS criteria. Together with the calculated dimensions of the mixing zone, two other options related to mixing zone calculations are provided by the discharge test. The three options are given below

- Real mixing zone dimensions based on AA-EQS or MAC-EQS criteria.
- The mixing zone acceptability based on a predefined default distances, which is calculated as $1/4 \cdot (4 \cdot \text{width} \cdot \text{length} / \pi)$ for the lake and for the other fresh waters as $L\text{-EQS} = \min(10 \cdot \text{width of water body}, \max(1000 \text{ m}))$ and $L\text{-MAC} = \min(0, 25 \text{ width of water body}, \max(25 \text{ m}))$.
- Freely chosen the dimensions of mixing zone and the concentration of pollutant at the defined distance was calculated.

In this project the first option was considered as the basis for proceeding to the next tier.

4.3 TIER 3

Tier 3 is recommended to be applied when Tier 2 results are uncertain with respect to meeting standards. Since the “Discharge Test” used in Tier 2 was originally designed for fresh waters and mixing zone acceptability was a matter of discussion, we decided to continue assessment. In Tier 3 the CORMIX model was used (CORMIX version 7.0).

4.4 CORMIX

CORMIX was chosen to investigate mixing zone design based on the specific requirements of the project given as follows:

- Predicts effluent dilution for coastal waters
- Provides the options of single port discharges located to the water surface CORMIX 3 and submerged port discharge CORMIX1, both were necessary in this project.
- Calculates densities of effluent discharge and receiving waters without the use of another model to calculate buoyancy and stratification effects.

- CORMIX is one of the models recommended by US EPA for mixing zone design. The results are given according to CCC and CMC criteria which can be easily converted to AA-EQS and MAC-EQS criteria.
- Gives detailed information about plume dilution, cumulative travelling time, plume thickness and width at the specified location where the EQS criteria are met. A visual tool for plume dilution is also provided.
- Allows for assumptions related to some parameters of discharge locations, which was quite important for this project.

CORMIX has been used in mixing zone calculation of municipal wastewater discharge to the Spokane River, Washington (LTI, 2002), prediction of Near-field dilution of wastewater effluents discharged to the Masan Bay (Kang et al., 1999), calculation of dilution of polycyclic aromatic hydrocarbons (PAH) in sea water (Hawboldt. K et al., 2006) evaluation of Donaustadt diffuser and mixing of the cooling water from discharges into the River Danube (Schmid, 2007). CORMIX is also one of the approved models by the Scottish Environment Protection Agency (SEPA) for calculation of initial dilution and mixing zones in coastal waters and estuaries (SEPA, 1998). Further information about CORMIX applications in different cases can be found online at <http://www.cormix.info/applications.php>.

In this project the visualization of the 3-D mixing graphs was provided from the CorVue tool (see Appendix 12). A general illustration of CORMIX inputs and outputs used in this project are shown at the following figure.

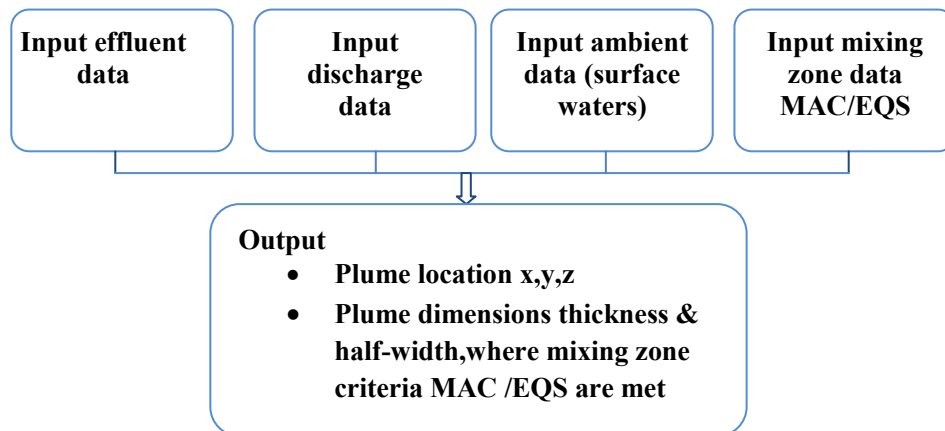


Figure 11. A general illustration of CORMIX model used at Tier 3 of Mixing Zone assessment.

4.4.1 Input data

The input data are divided in 4 sections which include effluent, ambient, discharge and mixing zone data.

Effluent data

The pollutant in the effluent discharge was assumed not to undergo any significant chemical or biological decay process therefore the pollutant type was considered conservative. Metal concentrations C_0 (mg/l) in the effluent flow were considered excess over the background concentration. Thus the background concentration of each metal was subtracted from the effluent metal concentration and the new obtained data were used as input in the CORMIX. The background concentration was also subtracted from EQS values. In this project, mixing zone calculations conducted using 2010 data.

Discharge concentration (mg/l) - At the first scenario total metal concentrations (mg/l) were used for all points (Appendix 1,2).

At the second scenario, mixing zone dilution was calculated using dissolved metal concentrations. Dissolved concentrations, however, were only available for the granulation water. Therefore data of unfiltered and filtered metals concentrations of 14 inland waters, 1 lake and 5 coastal Swedish waters (Köhler, 2010) were used to find a correlation between metals total and dissolved concentration for Cd, Ni, Pb. A K_{df} (dissolved factor) was estimated by dividing the mean filtered values of metal concentration with the unfiltered concentration.

Assuming that similar correlation exists in the discharge waters, dissolved metal concentrations were estimated from total metal concentrations times the calculated K_{df} values. These values for Cd, Ni and Pb were respectively 0.78, 0.21 and 0.78. Input data of dissolved metal concentration values are given at Appendix 3,4. The same results were obtained for the dissolved metal concentrations where the equation 10, recommended at Discharge Test was used

$$C_{total} = C_{dissolved} + \frac{K_p \cdot C_{ss} \cdot C_{dissolved}}{1000000} \quad \text{Equation 10}$$

where C_{total} is the total metal concentration (mg/l), $C_{dissolved}$ is dissolved metal concentrations (mg/l), C_{ss} is concentration of suspended solid in water (mg/l), K_p is partition coefficient between suspended solid and dissolved concentration (EU EQSD, 2010 c). K_p was calculated with Equation 11, where C_p sorbed metals concentrations, C_d dissolved metal concentration and TOC total organic carbon from (Köhler, 2010). TOC was used instead of C_{ss} as metal binding site (US EPA, 1996) in Equations 10 and 11.

$$K_p = \frac{C_p}{C_d \cdot TOC} \quad \text{Equation 11}$$

Due to the lack of data for Hg, K_{df} factor was calculated by dividing the mean value of reactive or easy reducible Hg with the mean total concentration of the dissolved fraction of 25 Swedish lakes (Lindström, 2001). The K_{df} value of Hg was 0.28. For granulation water the dissolved metal concentration were available from the measured data, directly from discharge water.

Flow Rate (m^3/s) - the same data as in “Discharge Test” the annual average flow rate (m^3/s) of each discharge point for 2010 (Table 6) were used as input.

Effluent density (kg/m^3) - was calculated based on the UNESCO equation set in the CORMIX. The effluent water in Rönnskär is collected at 13 m depth from the sea. Thus the effluent salinity was assumed to be almost the same with the sea water salinity 3 psu. In the UNESCO equation the salinity should be reported as part per thousands (ppt). Practical salinity does not have units and was assumed to be equivalent to ppt (Reid, 2006). Thus effluent densities were estimated using each effluent temperature (Table 1) and a salinity of 3 ppt. For discharge points 1, 4 and 4 West the water temperature varies within two limits. In those cases the density was calculated for the upper, lower and an average temperature value.

Ambient data

The actual cross-section of the ambient water body was required to be described as a rectangular channel. This channel was assumed to be uniform, literally “bounded” or “unbounded”. Therefore the first thing needed was the specification of the bounded and unbounded conditions.

The water body is considered bounded when both sides are constrained by banks as in streams, rivers or other similar water bodies (Donker & Jirka, 2007). For coastal waters, wide estuaries and wide lakes where the interaction of effluent plume with the far bank is almost impossible, the water body is specified as “unbounded” (Fig. 12). Thus the Bay of Bothnia was specified “unbounded”.

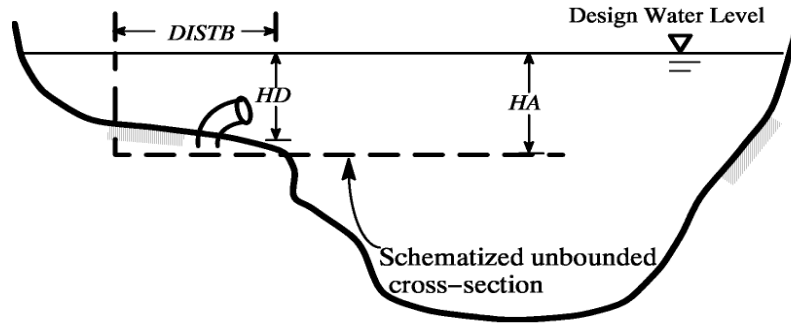


Figure 12. Example of schematization (or description of the water body as a rectangular cross-section) for the ambient input data in CORMIX, unbounded cross -section of the water body. From Donker (2008).

The Average depth - (HA) is the depth at the ambient water body (Fig. 12). Two assessments were done assuming two different average depths (Table 7).

Depth at discharge (m) - (HD) is the local depth of the water body near the discharge location (Fig. 12). For the CORMIX3 the HD values were assumed to be the same with HA. Whereas HD values for CORMIX 1(discharge point 4 and 4West and Sanitary water) were set (Table 7) due to the predefined criteria that actual depth should not differ from the average depth with more than ± 30 percent. A third scenario with different HD values based on the pipes location is used and the input data are shown at Appendix 7-8.

Wind speed (m/s) - (UV), considering all the information from the literatures a fixed value as yearly average wind speed was assumed in all the applications (Table 7).

Ambient Velocity (m/s) – the ambient conditions were considered steady and in this section the same ambient velocity of 0.05 m/s was used for all the discharges points. At Sanitary water in order the mixing to occur the ambient velocity was set 0.04 m/s; otherwise the model can't calculate the mixing in this case.

Ambient Average Density (kg/m^3) – was calculated at the same way as the discharge density the only difference in the input data was water temperature (Table 7). The yearly average ambient temperature obtained from Håkansson et al., (1996) was used for all the assessment.

Darcy-Weisbach friction factor f – was chosen to specify the ambient roughness. For the large lakes and coastal waters it varies from 0.02 to 0.03 (Donker & Jirka, 2007). A summary of all input ambient data is given at Table below

Table 7. Input ambient data for CORMIX 1 and CORMIX 3. Applied for two different average and discharge depths scenario

Models	Average depth (m)	Discharge depth (m)	Wind velocity (m/s)	Water velocity (m/s)	Temperature ($^{\circ}\text{C}$)	Darcy-Weisbach friction factor f
CORMIX 1	15	15	5	0.05	4.3	0.02
	5	5	5	0.05	4.3	0.02
CORMIX 3	15	11	5	0.05	4.3	0.02
	5	4	5	0.05	4.3	0.02

Discharge data

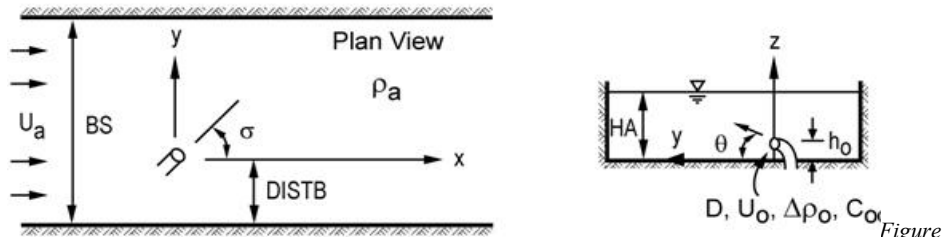
The discharge data required for CORMIX1 and CORMIX3 have a bit difference between them. CORMIX1 was used for submerged outlets; discharge points 4 and 4 West and Sanitary water. For the 1, 2, 3, and Granulation water discharge points with the outlets at the sea surfaces (Table1) was used CORMIX3.

Discharge data CORMIX 1

The nearest bank to the discharge points was chosen on the left side. The discharge distance from the nearest bank was 0 m and discharges were placed on the banks.

Vertical angle THETA(degrees) – which is the angle between the port center line and horizontal plane was 0 degree for points 4 and 4 West and Sanitary water , which shows that the discharges points horizontally.

Horizontal angle SIGMA (degrees) – is the angle between x-axis of the ambient current direction measured counterclockwise from the ambient to the plan projection of the port centerline. For discharges which point to the direction of ambient flow the sigma value is 0 degree (Fig 13). Assuming the same conditions the sigma value was set 0 degree.



13. Configuration of submerged one single discharge point where $HA=HD$.From Donker (2008)

Height of the Port center (m) – H_0 stands for the height of the discharge port center above the bottom and is used for submerged discharges. For discharges near the surface the H_0 can vary in the range $0.67 HD \leq H_0 \leq HD$. For the three discharge points the depth under the water surface was considered near the surface and the H_0 value was set 8 m and 3 m. For the scenario 4 the H_0 value is set 2.4m.

Discharge data CORMIX 3

Discharge location – location of discharge related with the nearest bank was chosen left for all the discharge outlets.

Discharge configuration – flush, protruding and co-flowing (Fig.14). Discharge in all the points was flush with the bank.

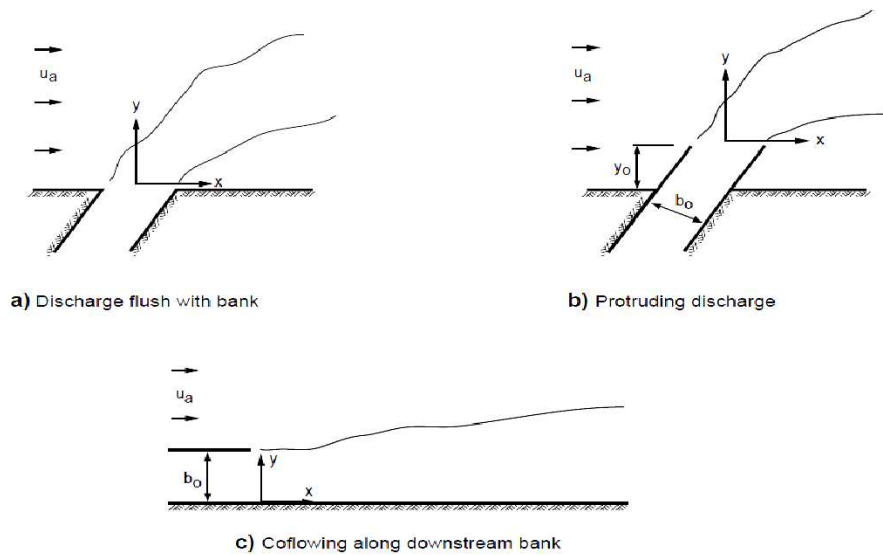


Figure 14. Discharge configuration of the flow channel related to the bank or shoreline used in CORMIX 3. From Donker & Jirka (2007).

Horizontal angle sigma (degrees) – is the angle between the discharge channel centerline with the downstream bank. The channels enter perpendicular to the bank and angle sigma used was 90 degrees (Fig. 15, a).

Bottom slope (degrees) – slope at the mouth of discharge was set at 15 degrees (Fig 15, b).

Local depth (m) – HD0 in front of the discharge outlet at the first assessment level was set at 10 m and in the second level at 3m for each of the outlets.

Discharge outlets – pipes diameter and bottom inverts depth are two parameters used for the discharge outlets

Diameter pipes (m) – the inner diameters pipes of each point (Table 1).

The bottom inverts depth (m) – H0 below the water surface. For the circular pipes CORMIX3 assumes that outlets flows full and are not submerged more than half of the outlet diameter. Therefore these values were set at the same value with the inner pipes diameter.

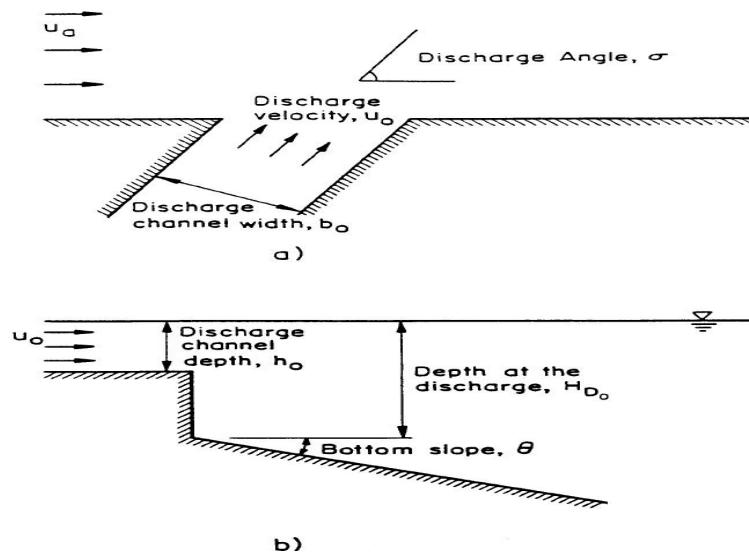


Figure 15. Discharge channel geometry for CORMIX 3 with a) the plan view and b) cross section view. From Jirka et al., (1996)

Mixing zone input data

The effluent type for the mixing zone was chosen as toxic. For toxic effluents two criteria are available in the CORMIX; CMC and CCC. The values of MAC-EQS are used for CMC values and AA-EQS for CCC criterion founded in Annex I of WFD (WFD 2008/105/EC). For Cd and Hg, different CMC and CCC were used but for Pb and Ni there is only one CCC criteria which was used for both cases. The final values of CCC and CMC were calculated as the excess over the background concentration (Table 8). The same procedure as in effluent metal concentration was followed. No mixing zones were specified and the region of interest at the first assessment was set at 1000 m. At the second assessment a default distance of 500 m from the discharge point was specified for the mixing zone. Therefore the dilution for each point was calculated using a mixing zone length maximum 500 m from the discharge point (regulatory mixing zone) and a region of interest (maximum distance where the dilution can be calculated) of 1000 m.

Table 8. Maximum concentration (MAC) and continues concentration criteria (AA-EQS) due to WFD and calculated (CMC) and (CCC) values for CORMIX

Metal type	Guideline MAC-EQS value (mg/l)	Guideline AA-EQS value (mg/l)	CORMIX CMC value (mg/l)	CORMIX CCC value (m/l)
Cd	0.00045	0.0002	0.000427	0.000177
Pb	-	0.0072	0.007133	0.007133
Hg	0.00007	0.00005	0.0000662	0.0000462
Ni	-	0.02	0.019161	0.019161

A summary of effluent, ambient and discharge input data is provided at Appendixes 1-8.

4.4.2 Outputs

After each simulation the output data are displayed follows:

- Session report
- Prediction file
- Flow classification
- Design recommendations
- Processing record

For this project we used only the outputs of the Session Report focusing on the mixing zone size. At the Session Report page there is a summary of the input data, parameters and mixing zones evaluations and hydraulics. Information about the Near – Field region conditions, buoyancy assessment, plume bank contact summary and information about CMC and CCC are included and are described as follows:

- The CMC or CCC criteria
- Corresponding dilution
- At which plume position, plume location (x,y,z) the criteria are met
- The plume dimension at this location, given as plume half-width (bh) and plume thickness (bv)
- Computed distance from the port opening to CMC or CCC location
- Dilution at Regulatory Mixing Zone, in second assessment set 500 m from discharge points

The output results of the mixing zone at CORMIX are given due to a coordinate system which is different for CORMIX 1 and CORMIX 3. The origin of the system in CORMIX 1 is located at a depth HD, at the bottom of receiving waters just below discharge pipe center. In CORMIX 3 the origin is located where the shoreline and discharge channel centerline intersect at the water surface (Jirka et al., 1996). The x–axis and y – axis lie in the horizontal plane. If we consider a discharge point in the river the x-axis points downstream at the direction of ambient flow and y-axis points to the left of an observer who looks downstream along the x-axis (Jirka et al., 1996). The z-axis points vertically upward. Even though, depending on the ambient currents or flow directions x–axis and y – axis interpretation can change. Bv is the thickness of the plume measured vertically and bh half-width measured horizontally in y – direction. Therefore based on this coordinative system CORMIX result as is mentioned even at Ragas,(2000) are defined as mixing zone length, maximum plume width and maximum cross – section area occupied by discharge plume.

4.4.3. Sensitivity Analysis

Sensitivity analysis in this project was performed based on two reasons

- Determine the effect of assumed average ambient parameters on the range of final results
- Check the sensitivity of model related to input parameters

For CORMIX1 and CORMIX3 sensitivity analysis were conducted separately. At the Appendixes 9 and 10 are given the input data used as the base case for sensitivity analysis. Parameters analyzed were ambient velocity, depth, temperature, discharge flow rate and effluent temperature. CorSens, available at CORMIX, was used for varying ambient velocity, depth and discharge flow rate. Additional model run were also conducted for changing the other parameters. Ambient velocity and discharge flow rate were varying by a factor of two. The other parameters were changed by a value ± 2 . The increase and decrease of the parameters was evaluated in the way how they affect mixing zone size. Results of sensitivity analysis are given at Tables 21-22.

4.5 Mixing zones overlapping

Discharge points 2 and 3 are very close to each other (Fig 16), but not at the same altitude related to the sea surface. Discharge outlet 2 is located above discharge outlet 3. Metal concentrations of point 2 can increase concentrations of point 3. Therefore an additional scenario was considered in this case.

- Calculation of a mixing zone for pipes 2 and 3, as effluent is discharged from one single outlet, pipe 3.

For this scenario metal concentrations were calculated with Equation 2. These values were used for estimation of mixing zones based on AA-EQS criteria. The determination of mixing zone length based on MAC-EQS criteria was done using the highest yearly concentration discharged from two points. Mixing zone was assessed for Cd concentration which was the common metal of concern for these two discharge points. Another assessment was done based on Hg concentration and MAC-EQS criteria. Estimation of mixing zones was done using Discharge Test and CORMIX3. In CORMIX3 despite the effluent concentration and flow rate all the parameters were set due to the second scenario for discharge point 3. Input data are given at Appendix 11.



Figure 16. Discharge point 2 at a higher level and discharge point 3 in the sea surface.

4.6 MIXING ZONE INVESTIGATION IN THE MINE AREA

4.6.1 Site description

Boliden mine is located 30 km Northwest of Skellefteå, in Västerbotten County, northern Sweden (Fig.17). The water from the Gillervattnet tailings pond is discharged to the Brubäcken creek. An artificial channel diverts discharged water from the Gillervattnet tailings pond to Brubäcken. In this system also a new lake called Nya Sjön, was created. The length of Brubäcken system that ends down at Skellefte River is 12 km (Lindström et al., 2001). Skellefte River is the largest river in the area with a length of 410 km.

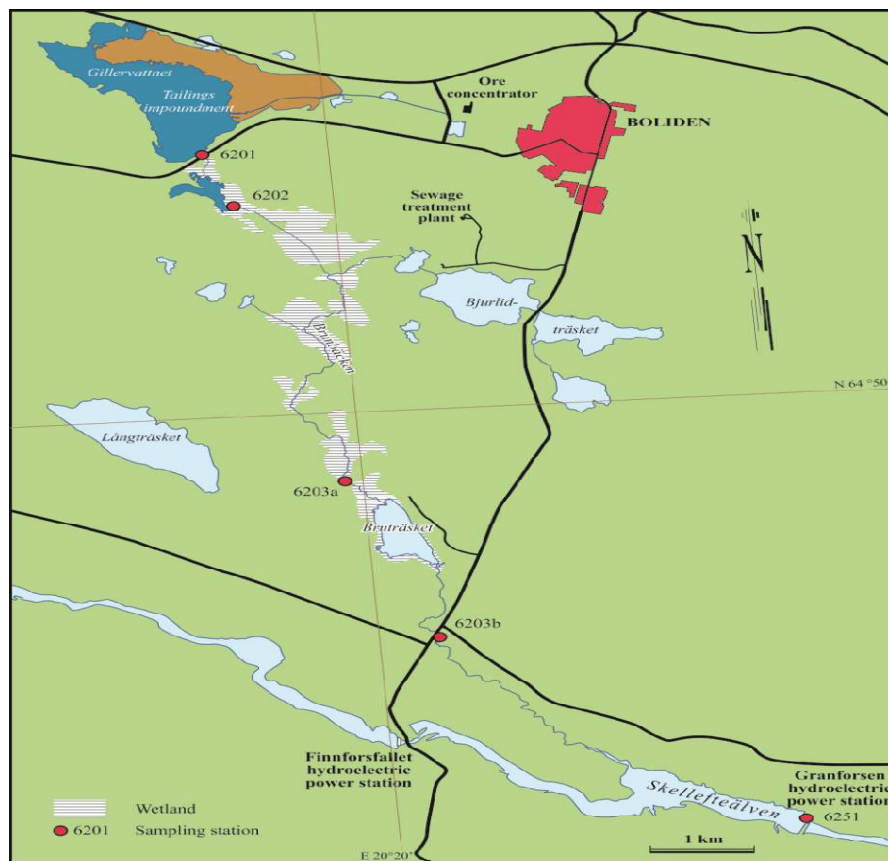


Figure 17. Brubäcken system and some of the sampling points. From Siergieiev, (2009).

Samples taken along whole Brubäcken system are used to check if the AA-EQS for priority substances are met in the creek. Moreover samples 6251 and 6250 were taken from the Skellefte River before and after mixing of creek water with the river. Figure 15 shows only point 6251. This was done to check if the mixing of creek water with river could increase the concentration of priority substances in river.

4.6.2 Materials and methods

Available data for points 6201 (outlet of the Gillervattnet tailings pond), 6202 (outlet of new lake), 6203 (a) and 6203 (b) (in the creek, Fig18) before discharge to the river were used. For the quality of river water the data of the points 6251 and 6250 were used. It was assumed that each point where the metal concentration was measured was a continuous point source or a discharge point. Therefore the first Tier of “Tiered Approach” in mixing zone guidelines was applied. The presence of Cd, Hg, Pb and Ni was checked for all the points. The annual average of total and dissolved metal concentration for year 2009 was compared with the AA-EQS and MAC-EQS for fresh water criteria (WFD, 2008/105/EC) in all the points. In the cases where the concentration was not available for 12 months, the mean value of available data was assumed as annual average value.



Figure 18. Sampling point 6203b, where the metal concentrations are measured at the discharge point to the stream

5. RESULTS

5.1 Tier 0 (statistical test results)

T-tests showed that more than one metal had concentrations exceeding AA-EQS values at 6 discharge point during 90% time of each year. At discharge point 2, only Cd exceeded EQS values. At all the other discharge points, more than one metal exceed EQS values (Table 9). For the granulation water, statistical tests were applied to the total and dissolved metal concentrations. In the case of total concentration the EQS values were exceeded for Cd, Ni and Pb. No exceedence of EQS values was registered for dissolved metal concentrations. Results also showed that except for point1, the AA-EQS values were exceeded by the same metals for all other discharges during 2009 and 2010.

Table 9. The metals that exceed EQS at each discharge point during 90% of the year (2008, 2009, and 2010 years).

Discharge outlets	Point 1	Point 2	Point 3	Point 4	Point 4 west	Granulation water	Sanitary water
YEAR 2008	Cd,Hg,	Cd	Cd, Hg	Cd, Hg	Cd	Cd,Ni, Pb	Cd, Hg, Pb, Ni
YEAR 2009	Cd	Cd	Cd, Hg	Cd	Cd, Hg	Cd,Ni,Pb	Cd, Hg, Pb, Ni
YEAR 2010	Cd, Pb	Cd	Cd, Hg	Cd	Cd, Hg	Cd, Ni, Pb	Cd, Hg, Pb, Ni

Results where yearly maximum concentrations of Cd and Hg have exceeded the respectively MAC-EQS values are shown at table10. Despite granulation water in all discharge points the Cd and Hg maximum concentration exceeded MAC-EQS criteria.

Table 10. Metals that exceed MAC-EQS criteria in 2010.

Discharge outlets	Point 1	Point 2	Point 3	Point 4	Point 4 west	Granulation water	Sanitary water
YEAR 2010	Cd, Hg	Cd,Hg	Cd, Hg	Cd,Hg	Cd, Hg	Cd	Cd, Hg

5.2 Tier 1

The location of discharge points related to the water surfaces was checked. The seven discharges were located at water surface or close to the sea surface (Table1). Therefore, probability for a low dilution rate was considered high.

5.3 Tier 2 Discharge Test

The discharge test allows for the assessment of the mixing zone size separately for each metal. Except for discharge point 2, where for AA-EQS criteria, there is only one mixing zone assessed due to Cd concentration, all discharge locations had more than one mixing zone. For example at discharge point 1, mixing zone assessment for 2010 was done based on both Pb and Cd concentrations and 2 mixing zones, with different sizes, were obtained (Table 9).

Two other aspects should be pointed out from the mixing zone results in the discharge test. In most of the discharge points the addition of background concentration was associated with an increase of the mixing zones length (Tables 11 and 12). This fact was more obvious in the Sanitary water.

The second item of note is related to the size of the receiving water body. The average width for the Gulf and Bay of Bothnia was considered to be the same, but the average depth and length are larger. For some discharges points, such as point 4 W for Hg concentrations, mixing zone dimensions are larger for Gulf of Bothnia which is logical based on the fact that discharge test consider the receiving water body size. However, some different results were noticed at the Sanitary water location where the calculated dimensions of mixing zones for all the cases in the Bay of Bothnia were larger than in Gulf of Bothnia even though the Bay of Bothnia is smaller. This may be related to the type of dominant mixing pattern in the effluent discharge, which in all cases was jet type except for the Sanitary water discharge. The dominant mixing pattern at Sanitary water was plume. For Sanitary water also the mixing zone length was high compared with the other discharges points. Even though the length of mixing zone in this case is larger than 1000 m, the model states that the dilution was enough to meet the EQS values for all metal concentrations.

Further the results of the discharge test showed that AA-EQS and MAC-EQS criteria were not met for Cd and Hg concentrations in discharge point 3. Both criteria were not also met at discharge point 4 for Cd concentration. Whereas at discharge point 1 the MAC-EQS criteria was not met only for Hg concentration. For Granulation water the dilution was not enough to meet the AA-EQS criteria for Pb concentration (Table 11,12).

The last results were the main reason for proceeding to the next level (Tier 3).

Table 11. Mixing zone dimensions registered by “Discharge test”, with data of 2010 and size of Gulf of Bothnia

Point-metal	L _{-mixing} (m)	L _{-mixing} (m) with background concentration
1-Cd _{MAC}	18	19
1-Cd _{EQS}	18	21
1-Hg _{MAC**}	-	-
1-Pb	8	8
2-Cd _{MAC}	12	13
2-Cd _{EQS}	8	9
2-Hg _{MAC}	4	4
3-Cd _{MAC**}	-	-
3-Cd _{EQS*}	551	551
3-Hg _{MAC**}	-	-
3-Hg _{EQS*}	551	551
4-Cd _{MAC**}	-	-
4-Cd _{EQS*}	553	553
4w-Cd _{MAC}	15	16
4w-Cd _{EQS}	15	17
4w-Hg _{MAC}	22	23
4w-Hg _{EQS}	17	18
Sanitary-Cd _{MAC}	7022	7795
Sanitary-Cd _{EQS}	2140	2731
Sanitary-Hg _{MAC}	77	86
Sanitary-Hg _{EQS}	29	34
Sanitary-Pb	381	382
Sanitary-Ni	634	691
Granulation-Cd _{MAC}	10	10
Granulation-Cd _{EQS}	5	6
Granulation-Pb*	551	551
Granulation-Ni	8	9

*In this case the mixing zone criterion was not met for EQS value and further assessment was needed.

**Mixing zone criteria were not met, discharge test doesn't show numerical results, and further assessment was needed

Table 12. Mixing zone dimensions registered by “Discharge test”, with data of 2010 and size of Bothnian Bay

Point -metal	L _{-mixing} (m)	L _{-mixing} (m) with background concentration
1-Cd _{MAC}	18	19
1-Cd _{EQS}	18	21
1-Hg _{MAC**}	-	-
1-Pb	8	8
2-Cd _{MAC}	12	13
2-Cd _{EQS}	8	9
2-Hg _{MAC}	4	4
3-Cd _{MAC**}	-	-
3-Cd _{EQS*}	393	393
3-Hg _{MAC**}	-	-
3-Hg*	393	393
4-Cd _{MAC*}	394	394
4-Cd _{EQS*}	553	553
4w-Cd _{MAC}	15	16
4w-Cd _{EQS}	15	17
4w-Hg _{MAC}	22	23
4w-Hg _{EQS}	16	17
Sanitary-Cd _{MAC}	9798	10877
Sanitary-Cd _{EQS}	2987	3810
Sanitary-Hg _{MAC}	55	61
Sanitary-Hg _{EQS}	41	48
Sanitary-Pb	532	542
Sanitary-Ni	885	964
Granulation-Cd _{MAC}	10	10
Granulation-Cd _{EQS}	5	6
Granulation-Pb*	393	393
Granulation-Ni	8	9

*In this case the mixing zone criterion was not met for EQS value and further assessment was needed.

**Mixing zone criteria were not met, discharge test doesn't show numerical results, and further assessment was needed

5.4 CORMIX RESULTS

Mixing zone parameters in CORMIX calculated for the total and dissolved metal concentrations are shown in Tables 13-20. The results give the information about the x-y-z position, width, thickness of plume /jet discharge and the rate of dilution where the AA-EQS and MAC-EQS criteria are met.

The third and fourth scenario results with dissolved metal concentrations but with different HA and HD values are shown in Tables 17-20.

In all applied scenarios the AA-EQS criteria were met within the default distance of 500 m. The MAC-EQS criteria have exceeded this distance only for Hg total concentration at discharge point 1 and 3 (Table 13). Buoyancy showed that all effluents were positively buoyant and tended to rise towards the water surface for all points.

Results for points 1, 4 and 4 west based on the three different effluent temperatures showed that dimensions of mixing zone for point 1, where CORMIX3 was used, are larger at highest temperature (Tables 13,16). For the other points where CORMIX1 was used changes in effluents temperature didn't have high effect in the plume dimensions (Table 14, 16).

Changes of the HA, HD and H0 has not a substantial effect on the mixing zone size especially for CORMIX 3 application. The high change in the average depth has obvious effect on the plume dimensions simulated by CORMIX 1. Therefore a high decrease on the average and outlet depth decrease size of the plume on vertical direction z and increase it toward x and y directions in horizontal plane (Tables 17-20).

5.4.1 Sensitivity Analysis Results

Effluent flow rate

The increase of effluent flow rate with a factor of two, effects x-y-z, bh and bv size where the AA-EQS criteria are met for point 1 (Table 21). This is more obvious in CORMIX 3, in the case of increase of effluent flow rate where mixing occurs more rapidly and the size of mixing zone decrease. For CORMIX1 the effect on the changes of flow rates is not very obvious (Table 22).

Effluent temperature

Change in effluent temperature with ± 2 °C in CORMIX3 showed that increase in temperature; increase the size of mixing zone.

Ambient average depth

Both CORMIX1 and CORMIX 3 were insensitive to the change of ambient average depth with ± 2 m.

Ambient velocity

Increase of ambient velocity with a factor of two has more effect on the increase of the x parameter in CORMIX3.

Ambient temperature

CORMIX 1 and CORMIX3 were insensitive to an ambient temperature changes with $\pm 2^{\circ}\text{C}$.

Table 13. Scenario 1, results of mixing zone dimensions where total metal concentrations is used as input data, model used CORMIX3

Discharge point – metals (temperature)	AA-EQS criterion was encounter at distance x (m)	AA-EQS criterion was encounter at distance y (m)	Half-width bh (m)	Thickness bv (m)	Dilution	MAC-EQS criterion was encounter at distance x (m)	MAC-EQS criterion was encounter at distance y (m)	Half- width bh (m)	Thickness bv (m)	Dilution
1-Cd(25°C)	138.83	0	84.07	0.14	4.1	130.86	0	81.06	0.13	3.786885
1-Cd (30°C)	146.75	0	96.78	0.12	4.1	138.21	0	93.29	0.11	3.786885
1-Cd (27.5°C)	142.94	0	90.57	0.13	4.1	134.60	0	87.30	0.12	3.786885
1-Hg(25°C) _{MAC}	-	-	-	-	-	532.11	0	202.80	0.64	46.15151
1-Hg(30°C) _{MAC}	-	-	-	-	-	573.08	0	235.80	0.55	46.15151
1-Hg(27.5°C) _{MAC}	-	-	-	-	-	553.28	0	219.70	0.59	46.15151
1-Pb(25°C)	5.71	-0.40	18.34	0.25	2.2	5.71	-0.40	18.34	0.25	1.602832
1-Pb(30°C)	8.88	-0.34	25.68	0.24	2.2	8.88	-0.34	25.68	0.24	1.602832
1-Pb (27.5°C)	6.95	-0.37	21.74	0.24	2.2	6.95	-0.37	21.74	0.24	1.602832
2-Cd (25°C)	2.91	-12.52	5.31	0.27	3.0	12.22	-24.78	11.35	-24.78	4.161593
2-Hg _{MAC} (25°C)	-	-	-	-	-	0.04	-2.16	1.08	0.36	1.457576
3-Cd	5.57	-28.89	11.78	0.58	3.8	8.66	-35.66	15.17	0.56	4.302108
3-Hg	449.72	-242.42	182.36	0.53	24.5	956.37	0	886.47	0.33	36.81818
Granulation -Cd	0.01	-0.51	0.66	0.40	1	-6.98	-0.13	22.41	0.12	2.053864
Granulation -Pb	265.26	0	151.96	0.15	9.99	265.26	0	151.96	0.15	9.992009
Granulation -Ni	5.99	-0.21	30.03	0.18	2.3	5.99	-0.21	30.03	0.18	1.696206

Table 14. Senario 1, results of mixing zone dimensions where total metal concentrations is used as input data, model used CORMIX1

Discharge point -metals temperature	AA-EQS criterion was encounter distance x (m)	AA-EQS criterion was encounter distance z (m)	Half-width bh (m)	Thickness bv (m)	Dilution	MAC-EQS criterion was encounter at distance x (m)	MAC-EQS criterion was encounter at distance z (m)	Half- width bh (m)	Thickness bv (m)	Dilution
4-Cd(15°C)	26.43	11	3.05	-	5.0	25.61	11	0.44	0.44	4.871194
4-Cd(25°C)	26.43	11	3.05	-	5.0	25.61	11	0.44	0.44	4.871194
4-Cd (20°C)	26.43	11	3.05	-	5.0	25.61	11	0.44	0.44	4.871194
4-Hg(15°C)	-	-	-	-	-	17.04	11	0.51	0.51	3.424242
4-Hg(25°C)	-	-	-	-	-	17.04	11	0.51	0.51	3.424242
4-Hg (20°C)	-	-	-	-	-	17.04	11	0.51	0.51	3.424242
4w-Cd(15°C)	3.83	10.25	0.71	-	4.3	3.65	10	0.34	0.34	3.927400
4w-Cd(25°C)	3.11	11	4.69	0.44	4.3	2.82	11	4.58	0.44	3.927400
4w-Cd(20°C)	3.19	11	3.09	0.66	4.3	2.86	11	2.87	0.66	3.927400
4w-Hg(15°C)	3.82	10.25	0.71	-	4.3	4.39	11	2.18	1.11	5.700000
4w-Hg(25°C)	3.10	11	4.68	0.44	4.3	4.07	11	5.07	0.46	5.700000
4w-Hg(20°C)	3.18	11	3.07	0.67	4.3	3.87	11	3.48	0.67	5.700000
Sanitary-Cd	4.33	9.96	0.56	-	44.2	5.69	11	0.94	1.24	74.88758
Sanitary-Ni	2.68	9.33	0.39	-	22.3	2.68	9.33	0.05	0.05	22.26976
Sanitary-Pb	2.20	9.12	0.33	-	16.7	2.20	9.12	0.08	0.08	16.72409
Sanitary-Hg	0.98	8.47	0.18	-	4.9	1.18	8.60	0.02	0.02	6.609091

Table 15. Scenario 2, results of mixing zone dimensions where dissolved metal concentrations is used as input data, model used CORMIX3

Discharge point –metals (temperature)	AA-EQS criterion was encounter at distance x (m)	AA-EQS criterion was encounter at distance y (m)	Half-width bh (m)	Thickness bv (m)	Dilution	MAC-EQS criterion was encounter at distance x (m)	MAC- EQS criterion was encounter at distance y (m)	Half-width bh (m)	Thickness bv (m)	Dilution
1-Cd (25°C)	118.30	0	76.16	0.12	3.4	-13.77	-0.04	6.41	0.06	2.950820
1-Cd (30°C)	124.35	0	87.46	0.11	3.4	-19.09	-0.03	8.83	0.05	2.950820
1-Cd (27.5°C)	121.44	0	81.94	0.12	3.4	-16.40	-0.04	7.57	0.06	2.950820
1-Hg (25°C)	-	-	-	-	-	288.82	0	134.31	0.27	12.92424
1-Hg (30°C)	-	-	-	-	-	310.28	0	155.67	0.23	12.92424
1-Hg (27.5°C)	-	-	-	-	-	299.85	0	145.24	0.25	12.92424
1-Pb (25°C)	0.03	-0.88	0.83	0.49	1	0.03	-0.88	0.83	0.49	1
1-Pb (30°C)	0.02	-0.75	0.85	0.49	1	0.02	-0.75	0.85	0.49	1
1-Pb (27.5°C)	0.02	-0.80	0.84	0.49	1	0.02	-0.80	0.84	0.49	1
2-Cd	0.77	-7.07	2.87	0.31	2.3	4.30	-14.98	6.47	0.26	3.245902
2-Hg _{MAC}	-	-	-	-	-	0.04	-2.15	0.76	0.25	1
3-Cd	2.00	-18.19	6.78	0.62	2.9	3.36	-22.88	8.91	0.60	3.355972
3-Hg	43.85	-80.40	40.28	0.45	6.8	144.08	-147.15	84.47	0.39	10.30303

Table 16. Scenario 2, results of mixing zone dimensions where dissolved metal concentrations is used as input data, model used CORMIXI

Discharge point -metals (temperature)	AA-EQS criterion was encounter at distance x (m)	AA-EQS criterion was encounter at distance z (m)	Half-width bh (m)	Thickness s bv (m)	Dilution	MAC-EQS criterion was encounter at distance x (m)	MAC-EQS criterion was encounter at distance z (m)	Half- width bh (m)	Thickness bv (m)	Dilution
4-Cd(15°C)	19.69	11	2.41	-	3.9	19.24	11	0.50	0.50	3.793911
4-Cd(25°C)	19.69	11	2.41	-	3.9	19.24	11	0.50	0.50	3.793911
4-Cd (20°C)	19.69	11	2.41	-	3.9	19.24	11	0.50	0.50	3.793911
4-Hg(15°C)	-	-	-	-	-	0	11	0.57	0.57	1
4-Hg(25°C)	-	-	-	-	-	0	11	0.57	0.57	1
4-Hg(20°C)	-	-	-	-	-	0	11	0.57	0.57	1
4w-Cd(15°C)	3.31	9.75	0.62	-	3.3	3.17	9.61	0.12	0.12	3.063232
4w-Cd(25°C)	2.06	10.22	0.49	-	3.3	1.98	10.05	0.36	0.36	3.063232
4w-Cd(20°C)	2.55	10.06	0.54	-	3.3	2.44	9.91	0.01	0.01	3.063232
4w-Hg(15°C)	1.69	8.15	0.40	-	1.1	2.17	8.58	0.16	0.16	1.590909
4w-Hg(25°C)	1.09	8.28	0.32	-	1.1	1.38	8.82	0.32	0.32	1.590909
4w-Hg(20°C)	1.31	8.21	0.36	-	1.1	1.68	8.72	0.32	0.32	1.590909
Sanitary-Cd	3.63	9.71	0.49	-	34.5	5.29	10.28	0.00	0.00	58.54800
Sanitary-Ni	2.26	9.15	0.34	-	17.4	2.26	9.15	0.08	0.08	17.35749
Sanitary-Pb	0.79	8.34	0.15	-	3.5	0.79	8.34	0.08	0.08	3.505958
Sanitary-Hg	0.41	8.05	0.10	-	1.3	1.18	8.60	0.02	0.02	6.609091

Table 17. Senario3. results of mixing zone dimensions where dissolved metal concentrations are used as input data and HA, HD values are 5m. Model used is CORMIX3

Discharge point -metals (temperature)	AA-EQS criterion was encounter at distance x (m)	AA-EQS criterion was encounter at distance y (m)	Half-width bh (m)	Thickness bv (m)	Dilution	MAC-EQS criterion was encounter at distance x (m)	MAC- EQS criterion was encounter at distance y (m)	Half-width bh (m)	Thickness bv (m)	Dilution
1-Cd (27.5°C)	121.44	0	81.94	0.12	3.4	-16.40	-0.04	7.57	0.06	2.950820
1-Hg (27.5°C)	-	-	-	-	-	299.32	0	145.07	0.25	12.87878
1-Pb(27.5°C)	0.02	-0.80	0.84	0.49	1	0.02	-0.80	0.84	0.49	1
2-Cd	0.77	-7.07	2.87	0.31	2.3	4.27	-14.88	6.43	0.26	3.231850
2-Hg	-	-	-	-	-	0.04	-2.14	0.76	0.25	1
3-Cd	2.02	-18.19	6.78	0.62	2.9	3.39	-22.89	8.91	0.60	3.355972
3-Hg	44.21	-80.38	40.30	0.45	6.8	145.06	-146.74	84.44	0.39	10.30303

Table 18 . Scenario3, results of mixing zone dimensions where dissolved metal concentrations are used as input data and HA, HD and H0 values are respectively 5, 4m and 3m. Model used is CORMIXI

Discharge point –metals (temperature)	AA-EQS criterion was encounter at distance x (m)	AA-EQS criterion was encounter at distance z (m)	Half-width bh (m)	Thickness s bv (m)	Dilution	MAC-EQS criterion was encounter at distance x (m)	MAC-EQS criterion was encounter at distance y (m)	MAC-EQS criterion was encounter at distance z (m)	Half- width bh (m)	Thickness bv (m)	Dilution	
4-Cd(20°C)	19.76	0	4	2.41	-	3.9	19.31	0	4	0.39	0.39	3.793911
4-Hg(20°C)	-	-	-	-	-	-	0	0	4	0.57	0.57	1
4w-Cd(20°C)	16.57	1	4	11.31	0.23	3.3	11.09	1	4	8.94	0.27	3.063232
4w-Hg(20°C)	1.32	0	3.22	0.36	-	1.1	1.88	0	4	2.59	0.31	1.590909
Sanitary-Cd	16.98	1	4	4.71	0.26	34.6	1.10	0	3.55	0.05	0.05	5.854801
Sanitary-Ni	2.94	1	4	2.01	0.30	17.4	2.94	1	4	2.01	0.30	17.4
Sanitary-Pb	0.80	0	3.35	0.15	-	3.5	0.80	0	3.35	0.01	0.01	3.504837
Sanitary-Hg	0.42	0	3.05	0.10	-	1.3	0.52	0	3.14	0.06	0.06	1.818182

Table 19. Senario4, results of mixing zone dimensions where dissolved metal concentrations are used as input data with HA, HD and H0 values set due to pipes's depth and diameters. Model used is CORMIXI

Discharge point -metals (temperature)	AA-EQS criterion was encounter at distance x (m)	AA-EQS criterion was encounter at distance y (m)	Half-width bh (m)	Thickness bv (m)	Dilution	MAC-EQS criterion was encounter at distance x (m)	MAC- EQS criterion was encounter at distance y (m)	Half-width bh (m)	Thickness bv (m)	Dilution
1-Cd (27.5°C)	-18.17	-0.01	6.49	0.04	3.2	-16.40	-0.04	7.57	0.06	2.950820
1-Hg (27.5°C)	-	-	-	-	-	299.33	0	145.07	0.25	12.87878
1-Pb(27.5°C)	0.02	-0.80	0.84	0.49	1	0.02	-0.80	0.84	0.49	1
2-Cd	0.87	-7.08	2.88	0.31	2.3	4.71	-14.94	6.47	0.26	3.231850
2-Hg	-	-	-	-	-	0.04	-2.14	0.76	0.25	1
3-Cd	2.23	-18.20	6.78	0.62	2.9	3.71	-22.91	8.92	0.60	3.355972
3-Hg	47.01	-79.93	40.25	0.45	6.8	151.49	-143.31	83.88	0.39	10.30303

Table 20. Senario4, results of mixing zone dimensions where dissolved metal concentrations are used as input data with HA, HD and H0 values set due to the pipes's depth and diameters. Model used is CORMIXI

Discharge point –metals (temperature)	AA-EQS criterion was encounter at distance x (m)	AA-EQS criterion was encounter at distance z (m)	Half-width bh (m)	Thicknes s bv (m)	Dilution	MAC-EQS criterion was encounter at distance x (m)	MAC-EQS criterion was encounter at distance y (m)	MAC-EQS criterion was encounter at distance z (m)	Half- width bh (m)	Thickness bv (m)	Dilution
4-Cd(20°C)	19.77	0	3	2.41	-	3.9	19.32	0	3	0.52	3.793911
4-Hg(20°C)	-	-	-	-	-	-	0	0	3	0.57	1
4w-Cd(20°C)	37.82	1	3	17.60	0.15	3.3	31.45	1	3	15.93	3.063232
4w-Hg(20°C)	1.32	0	2.62	0.36	-	1.1	2.09	0	3	2.82	1.590909
Sanitary-Cd	22.41	1	3	5.40	0.22	34.5	1.02	0	3	0.38	5.854801
Sanitary-Ni	12.35	1	3	3.88	0.16	17.4	12.35	1	3	3.88	17.4
Sanitary-Pb	0.80	0	2.75	0.15	-	3.5	0.80	0	2.75	0.15	3.5
Sanitary-Hg	0.42	0	2.45	0.10	-	1.3	0.53	0	2.54	0.03	1.818182

Table 21. Results of sensitivity analysis, CORMIX3 with the dissolved metals concentrations for year 2010, made for point 1- Cd , temperature 25°C, from scenario 2

Sensitivity analysis scenarios	AA-EQS (EQS) criterion was encounter at distance x (m)	AA-EQS (EQS) criterion was encounter at distance y (m)	Half- width bh (m)	Thickness bv (m)	Dilution	MAC-EQS criterion was encounter at distance x (m)	MAC-EQS criterion was encounter at distance y (m)	Half- width bh (m)	Thickness bv (m)	Dilution
Main scenario	118.30	0	76.16	0.12	3.4	-13.77	-0.04	6.41	0.06	2.950820
Flow rate x 2	6.84	-27.14	13.12	0.39	3.4	3.80	-20.43	9.66	0.41	2.950820
Flow rate /2	80.22	0	47.45	0.10	3.4	-7.12	-0.03	3.44	0.05	2.950820
Effluent temperature +2 °C	120.73	0	80.78	0.12	3.4	-15.59	-0.04	7.26	0.06	2.950820
Effluent temperature -2 °C	115.71	0	71.33	0.13	3.4	-11.72	-0.04	5.55	0.07	2.950820
Average depth +2	118.30	0	76.16	0.12	3.4	-13.77	-0.04	6.41	0.06	2.950820
Average depth -2	118.30	0	76.16	0.12	3.4	-13.77	-0.04	6.41	0.06	2.950820
Ambient velocity x2	134.22	0	42.59	0.11	3.4	-3.09	-0.07	1.50	0.08	2.950820
Ambient velocity /2	56.19	0	157.38	0.33	3.7	-93.00	-0.03	39.63	0.13	2.950820
Ambient temperature +2 °C	117.49	0	74.52	0.13	3.4	-13.51	-0.04	6.32	0.06	2.950820
Ambient temperature -2 °C	117.94	0	75.35	0.13	3.4	-13.68	-0.04	6.42	0.06	2.950820

Table 22. Results of sensitivity analysis, CORMIX1 with the dissolved metal concentrations for year 2010, made for point 4- Cd ,from scenario 2.

Sensitivity analysis scenarios	AA-EQS criterion was encounter at distance x (m)	AA-EQS criterion was encounter at distance z (m)	Half-width bh (m)	Thickness bv (m)	Dilution	MAC-EQS criterion was encounter at distance x (m)	MAC- EQS criterion was encounter at distance z (m)	Half- width bh (m)	Thicknes s bv (m)	Dilution
Main scenario	19.69	11	2.41	-	3.9	19.24	11	0.50	0.50	3.793911
Flow rate x 2	19.86	11	2.51	-	3.9	19.41	11	0.23	0.23	3.793911
Flow rate /2	19.48	11	2.26	-	3.9	19.03	11	0.01	0.01	3.793911
Effluent temperature +2 °C	19.69	11	2.41	-	3.9	19.24	11	0.50	0.50	3.793911
Effluent temperature -2 °C	19.69	11	2.41	-	3.9	19.24	11	0.50	0.50	3.793911
Average depth +2	19.69	11	2.41	-	3.9	-	-	-	-	-
Average depth -2	19.69	11	2.41	-	3.9	19.24	11	0.50	0.50	3.793911
Ambient velocity x2	19.48	11	2.26	-	3.9	19.03	11	0.01	0.01	3.793911
Ambient velocity /2	19.86	11	2.51	-	3.9	6.11	11	0.31	0.31	1.604215
Ambient temperature +2 °C	19.69	11	2.41	-	3.9	19.24	11	0.50	0.50	3.793911
Ambient temperature -2 °C	19.69	11	2.41	-	3.9	19.24	11	0.50	0.50	3.793911

5.5 Mixing zones overlapping

The results of mixing zone for points 2 and 3 are given at Tables 23 and 24. The discharge test showed that the MAC and EQS criteria of mixing zone is not met in this case. Whereas CORMIX results (Table 24) showed that AA-EQS criteria is met within a short distance from the discharge point.

Table 23. Results of Discharge Test for point 3 at the mixing zone overlapping case , receiving water body , Bothnian Bay

Point –metal	L _{Mixing} (m)	L _{Mixing} (m) with background concentration
3-Cd _{MAC}	-	-
3-Cd _{EQS}	393	393
3-Hg _{MAC}	-	-

Table 24.Pipe 2 and 3 overlapping, results of mixing zone dimensions where dissolved metal concentrations is used as input data, model used CORMIX

Discharge point –metals (temperature)	AA-EQS criterion was encounter at distance x (m)	AA-EQS criterion was encounter at distance y (m)	Half-width bh (m)	Thickness bv (m)	Correspond ing dilution	MAC-EQS criterion was encounter at distance x (m)	MAC- EQS criterion was encounter at distance y (m)	Half-width bh (m)	Thickness bv (m)	Correspond ing dilution
3-Cd	1.19	-15.97	5.12	0.79	2.9	2.29	-21.01	7.20	0.77	3.348946
3-Hg _{MAC}	-	-	-	-	-	106.20	-137.76	73.43	0.51	10.257576

5.6 Results for the mine area

In both cases where the total and the dissolved metal concentration were used the metal concentration didn't exceed the AA-EQS and MAC-EQS criteria. The same results were obtained even for the concentration measured upstream and downstream the river in points 6251 and 6250. The possibility that the dilution was enough to meet the EQS values at the measured points is high.

6. DISCUSSION

This project presents the mixing zone investigation and estimation based on Mixing Zone Guideline. Therefore a Tiered Approach was used for determination of mixing zones on seven discharge points in Rönnskär Smelter and also in Boliden mine area. For the mine area, results showed that no mixing zone design was necessary. Discharge Test was used at Tier 2 for determination of mixing zones length in Rönnskär Smelter. Whereas more sophisticated results related to mixing zone length and discharge plume size were obtained by CORMIX model at Tier 3. For the discharge points where more than one metal was a matter of concern the estimation of mixing zones was done separately case by case.

For all concentrations in points 2, 4 W, for Cd concentration in point 1 and for Cd and Ni concentrations in Granulation water the discharge test showed that dilution was enough to meet the EQS criteria. In Sanitary water the EQS criteria for Cd concentrations was met at a distance larger than 1000 m. Further investigations were needed after Discharge Test application for points 3, 4, for Pb concentration in Granulation water and point 1 for Hg concentration. Also in Sanitary water for Cd concentration a better estimation of mixing was needed.

Even though the main data used in the project were monthly metal concentrations as is required at WFD (WFD 2008/105/EC), uncertainties related to comparison of total concentrations with EQS values set using dissolved values remain. In addition, in chemical analysis for the metal dissolved fractions there is always risk of the adsorption to the container walls and underestimation of the dissolved metals concentration. Therefore when the expected metal concentrations are below EQS values the analyzed total metals concentration can be compared with respectively EQS values (Quevauviller et al., 2008). But when the total metal fraction is high compared to the dissolved fraction, this can lead to an overestimation of exceedence of the EQS value. This is the case for the granulation water where the total metal concentration exceeds the EQS values for Cd, Ni and Pb (Table 9). Further for Pb concentration, the assessment of mixing zones was needed until Tier 3 (Table 11, 12). When the dissolved metal concentrations were compared with EQS values, the statistical test showed no exceedence of EQS values for all the metals. Therefore the use of total metal concentration instead of dissolved until Tier 3 may be too conservative leading to the unnecessary limitations.

Moreover bioavailability of the metals related to PH, water hardness, Ca, Mg concentration and DOC is another matter that should be considered. Although the dissolved concentration of metals can exceed the EQS values, the labile or bioavailable fraction has been shown to be lower than EQS values (Unsworth et al., 2009). Even the Biotic Ligand Models (BLM) for estimation of toxic fraction of metals in fresh water, have shown an overestimation of metal toxicity in relation to EQS values for some metals such as Cu or Zn (Comber et al., 2008). The use of BML models as a sub-step to the tiered approaches for the metals effluents in Swedish

waters is recommended in one of the studies by the Swedish Environmental Research Institute (Cousins.A.P et al., 2009).

Another issue related to EQS values is the metal background concentrations. The importance of taking into account the background concentration is emphasized at Comber et al., (2008). Further when metal concentrations exceed EQS values it is required from member states to consider natural background concentrations (WFD 2008/105/EC). A mean value of total metal concentrations considered as a background, upstream concentration in the Discharge Test showed that a background concentration affects the mixing zone length. This still remains a matter of discussion if the bioavailable fraction of metals, dissolved or total concentration will be considered in the natural, background and upstream concentrations. In the Netherlands, for a generic background concentrations of Cadmium are used two values 0.2 µg/l for inland waters and 0.62µg/l for other waters taking into account water hardness and bioavailability (EU EQSD, 2010, b). Based on the characteristics of Swedish waters, a common value can be used for metals background concentration where the mixing zone guidelines are applied. (But this may need to be more flexible due to the larger variability in surface waters and natural source areas across Sweden). Therefore more investigation is needed related to local background concentration before mixing zone applications. Further researches should be also undertaken for cases where background or natural metal concentration is close or equal to EQS values. Special consideration or site specific approaches should be use in these cases. Even though the Discharge Test is designed for a rough estimation of mixing zone length considering the total metal concentration, can lead to overestimation of mixing zone length required.

The lack of a specific option for coastal waters and approximations used in this project can also lead to uncertainties in results. This can be seen at Sanitary water results (Table 11,12) where mixing zone size exceed the default value (1000m). Even though the final results shows that mixing is enough to meet the criteria for this point. Although this can be related to discharge type which is only in this point plume, diameter pipe and hydraulic aspects, the final results lead to uncertainties.

Thus, for coastal waters in Tier 2 an adjustment of Discharge Test or a similar model with the same data requirements but less sophisticated than CORMIX should be use. Therefore a common approach can be use for inland and coastal waters at the same level of mixing zones assessment. Whereas in this project the comparison of results of Discharge Test and CORMIX for the total metal concentrations is unfair and almost impossible since both models are designed for different assessment levels. Changes in the mean ambient flow rate can also lead to different mixing zone length determinations. Further CORMIX in this project and in other assessments (L.T.I 2002) has shown to be sensitive to ambient velocity.

Therefore some seasonal scenarios can help in an approximation of results with reality. Summer and winter conditions are considered in estimation of mixing zone by CORMIX at L.T.I (2002). Hence, the size of the mixing zone partly depends on the hydrodynamics of the receiving waters such as flow rate or currents speed, wind velocity and water depth which affect mixing. Thus, temporal variability of ambient conditions may have effects on the mixing zone size. In the mixing zone guidelines seasonal permit conditions are also discussed for Scandinavia, since frozen fresh

water or water covered by ice can have drastic difference in mixing zone size, dilution and plume trajectory (Huttula et al., 1998). But a more detailed study is needed in those cases. Moreover in northern Sweden, water flows and the properties can vary due to the snow melting in May-July which effects even the dilution and the concentration of trace metals on the receiving waters (SWECO, 2008). The effects of temporal variation in trace metal concentrations has also been shown in other coastal waters (Hatje et al., 2001). This may be taken into account also in the background concentration.

In this project the mixing zone size for different metals present in the same effluent is determined separately and independently in each case based only on their EQS values. Indeed these substances are not independent since they undergo through same physical dilution (EU EQSD, 2010, a).

Metals complexes after mixing with receiving waters may be effected in different ways by water temperatures, photochemical reactions and other processes which are not considered here. Effluents in this case can be considered as a mixture of trace metals which can have antagonistic or synergistic effects to each other and varying level effects on aquatic life.

Moreover in some effluents of the project despite the priority substances there is also the presence of Zn and other metals. At high concentrations and together with more toxic metals, Zn may also have antagonist/cumulative effects on the toxicity of other metals. This was mentioned by Lydersen et al. (2011) and used as an assumption at Lindeström's (1988) investigation. Presence of Zn has shown antagonistic action to Cd uptake in the fresh water fish (Kargin & Çogun, 1999, Hemelraad et al. 1987). This fact can be taken into account to produce better results of mixing zone and closer to the real effect on aquatic life.

Thus, aiming to find out the real impacts of metals on the aquatic life and biota we came up at the same conclusion that further research is needed when more than one metal are present at the same effluent discharge.

Hence, considering the hydraulic aspects of the mixing zone assessment the outlet position related to the water surface has also effect on the mixing zone size. In this study, where all the effluents were buoyant, for the outlets located beneath water, the mixing zone size in horizontal plan resulted to be smaller. Thus in the mixing zone application for the coastal waters outlets positions related to the water surface, can prevent the effluent impact on the shoreline, on the sea bed and effect the size of the mixing zone. Moreover the design of the effluent pipes has also shown to have a high effect on the mixing zone size (Bleninger et al., 2005). Therefore, despite the common approach, for each mixing zone design detailed assessments related even to the hydraulic factors which cause a better mixing and a reduce the size of the mixing zone are needed.

7. CONCLUSION

This study showed that mixing zone guidelines can be apply for different discharge points as in Rönnskär smelter. In this project the estimation of the mixing zone for the

effluents that contain more than one metal was done independently. Results of CORMIX1 and CORMIX2 concluded that calculated dilution was enough to meet the AA-EQS for each metal within 500 m distance from each discharge point. Even though the determination of mixing zone was done until Tier3 and a sophisticated dilution model was used there is still place for uncertainties. For better results, the dissolved concentration of the metals should be considered from the first step of the mixing zone assessment. Further investigation on the mixing zone design and evaluation of the Mixing Zone Guidelines are needed in order to come up with similar results and produce some common scenarios and solutions. More field investigations for fresh and coastal waters, cooperation of different institutions, and organization of similar projects at different sites in Sweden can lead to a common approach of mixing zone application. Therefore such regulations based on the Swedish surface waters characteristics, metal background or natural concentrations, climate conditions and other specific factors should be set if the Mixing Zone Guidelines is going to be used for protection of aquatic and human life in Swedish waters.

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APENNDIX I

Appendix I. Input data of CORMIX3 with the total metal concentrations for year 2010, scenario I.

Scenario I		Effluent characteristics				Ambient characteristics				Discharge characteristics				
Discharge point - metals	Discharge - concentration (mg/l)	Flow rate (m3/s)	Temperature -re (°C)	Average -e depth HA(m)	Depth at discharge HD (m)	Ambie- nt velocit- y (m/s)	Wind speed (m/s)	Tempe -rature (°C)	Darcy friction	Horizo -ntal angle	Bottom slope	Local depth (m)	Pipe diameter (m)	Bottom invert depth (m)
1-Cd _{MAC}	0.001617	0.14	25,30,27.5	15	15	0.05	5	4.3	0.02	90	15	10	1	1
1-Cd _{EQS}	0.000717	0.14	25,30,27.5	15	15	0.05	5	4.3	0.02	90	15	10	1	1
1-Hg _{MAC}	0.003046	0.14	25,30,27.5	15	15	0.05	5	4.3	0.02	90	15	10	1	1
1-Pb	0.011433	0.14	25,30,27.5	15	15	0.05	5	4.3	0.02	90	15	10	1	1
2-Cd _{MAC}	0.001777	0.0893	25	15	15	0.05	5	4.3	0.02	90	15	10	0.6	0.6
2-Cd _{EQS}	0.000527	0.0893	25	15	15	0.05	5	4.3	0.02	90	15	10	0.6	0.6
2-Hg _{MAC}	0.000096	0.0893	25	15	15	0.05	5	4.3	0.02	90	15	10	0.6	0.6
3-Cd _{MAC}	0.001837	0.397	25	15	15	0.05	5	4.3	0.02	90	15	10	1	1
3-Cd _{EQS}	0.000677	0.397	25	15	15	0.05	5	4.3	0.02	90	15	10	1	1
3-Hg _{MAC}	0.00243	0.397	25	15	15	0.05	5	4.3	0.02	90	15	10	1	1
3-Hg _{EQS}	0.001126	0.397	25	15	15	0.05	5	4.3	0.02	90	15	10	1	1
Granulation Cd _{MAC}	0.000877	0.1125	40	15	15	0.05	5	4.3	0.02	90	15	10	1	1
Granulation Cd _{EQS}	0.000177	0.1125	40	15	15	0.05	5	4.3	0.02	90	15	10	1	1
Granulation Pb	0.071273	0.1125	40	15	15	0.05	5	4.3	0.02	90	15	10	1	1
Granulation Ni	0.032501	0.1125	40	15	15	0.05	5	4.3	0.02	90	15	10	1	1

Appendix 2. Input data of CORMIX1 with the total metal concentrations for year 2010, scenario I

Scenario 1	Effluent characteristics				Ambient characteristics				Discharge characteristics						
	Discharge point –	Discharge- concentra- tion	Flow rate (m3/s)	Temperat- ure (°C)	Average depth HA(m)	Depth at dischar- ge HD (m)	Ambie nt velocit- y (m/s)	Wind speed (m/s)	Tempe- rature (°C)	Darcy friction	Horizo- ntal angle	Vertica- l angle	Distanc- e to the nearest bank (m)	Pipe diameter (m)	Discharge port height (m)
	4-Cd _{MAC}	0.00208	1.12	15,25, 20	15	11	0.05	5	4.3	0.02	0	0	1	0.8	8
	4-Cd _{EQS}	0.000887	1.12	15,25, 20	15	11	0.05	5	4.3	0.02	0	0	1	0.8	8
	4-Hg _{MAC}	0.000226	1.12	15,25, 20	15	11	0.05	5	4.3	0.02	0	0	1	0.8	8
	4west-Cd _{MAC}	0.001677	0.04	15,25,20	15	11	0.05	5	4.3	0.02	0	0	1	0.8	8
	4west-Cd _{EQS}	0.000757	0.04	15,25,20	15	11	0.05	5	4.3	0.02	0	0	1	0.8	8
	4west-Hg _{MAC}	0.000376	0.04	15,25,20	15	11	0.05	5	4.3	0.02	0	0	1	0.8	8
	4west-Hg _{EQS}	0.000196	0.04	15,25,20	15	11	0.05	5	4.3	0.02	0	0	1	0.8	8
	Sanitary-Cd _{MAC}	0.031977	0.0014	18	15	11	0.04*	5	4.3	0.02	0	0	1	0.2	8
	Sanitary-Cd _{EQS}	0.007827	0.0014	18	15	11	0.04*	5	4.3	0.02	0	0	1	0.2	8
	Sanitary-Hg _{MAC}	0.000436	0.0014	18	15	11	0.04*	5	4.3	0.02	0	0	1	0.2	8
	Sanitary-Hg _{EQS}	0.000226	0.0014	18	15	11	0.04*	5	4.3	0.02	0	0	1	0.2	8
	Sanitary-Ni	0.426711	0.0014	18	15	11	0.04*	5	4.3	0.02	0	0	1	0.2	8
	Sanitary-Pb	0.119293	0.0014	18	15	11	0.04*	5	4.3	0.02	0	0	1	0.2	8
	Sanitary-Hg	0.000226	0.0014	18	15	11	0.04*	5	4.3	0.02	0	0	1	0.2	8

*For all the cases in Sanitary water CORMIX1 required an ambient velocity lower than 0.05 m/s. Therefore an ambient velocity of 0.04m/s was used in Sanitary water calculations

Appendix 3. Input data of CORMIX3 with the dissolved metal concentrations for year 2010, scenario 2

Scenario 2		Effluent characteristics				Ambient characteristics				Discharge characteristics				
Discharge point	Discharge concentration (mg/l)	Flow rate (m3/s)	Temperature (°C)	Average depth HA(m)	Depth at discharge HD (m)	Ambient velocity (m/s)	Wind speed (m/s)	Temperature (°C)	Darcy friction	Horizontal angle	Bottom slope	Local depth (m)	Pipe diameter (m)	Bottom invert depth (m)
1-Cd _{MAC}	0.00126	0.14	25, 20, 27.5	15	15	0.05	5	4.3	0.02	90	15	10	1	1
1-Cd _{EQS}	0.0006	0.14	25, 20, 27.5	15	15	0.05	5	4.3	0.02	90	15	10	1	1
1-Hg _{MAC}	0.00853	0.14	25, 20, 27.5	15	15	0.05	5	4.3	0.02	90	15	10	1	1
1-Pb	0.0024	0.14	25,20,27.5	15	15	0.05	5	4.3	0.02	90	15	10	1	1
2-Cd _{MAC}	0.001386	0.0893	25	15	15	0.05	5	4.3	0.02	90	15	10	0.6	0.6
2-Cd _{EQS}	0.000405	0.0893	25	15	15	0.05	5	4.3	0.02	90	15	10	0.6	0.6
2-Hg _{MAC}	0.000027	0.0893	25	15	15	0.05	5	4.3	0.02	90	15	10	0.6	0.6
3-Cd _{MAC}	0.001433	0.397	25	15	15	0.05	5	4.3	0.02	90	15	10	1	1
3-Cd _{EQS}	0.000522	0.397	25	15	15	0.05	5	4.3	0.02	90	15	10	1	1
3-Hg _{MAC}	0.00068	0.397	25	15	15	0.05	5	4.3	0.02	90	15	10	1	1
3-Hg _{EQS}	0.000313	0.397	25	15	15	0.05	5	4.3	0.02	90	15	10	1	1

Appendix 4. Input data of CORMIX1 with dissolved metal concentrations for year 2010, scenario 2

Scenario 2		Effluent characteristics				Ambient characteristics				Discharge characteristics				
Discharge point -metals	Discharge concentration (mg/l)	Flow rate (m ³ /s)	Temperature (°C)	Average depth HA(m)	Depth at discharge HD (m)	Ambient velocity (m/s)	Wind speed (m/s)	Temperature (°C)	Darcy friction	Horizontal angle	Vertical angle	Distance to the nearest bank (m)	Pipe diameter (m)	Discharge port height (m)
4-Cd _{MAC}	0.001433	1.12	15,25,20	15	11	0.05	5	4.3	0.02	0	0	1	0.8	8
4-Cd _{EQS}	0.000685	1.12	15,25,20	15	11	0.05	5	4.3	0.02	0	0	1	0.8	8
4-Hg _{MAC}	0.00068	1.12	15,25,20	15	11	0.05	5	4.3	0.02	0	0	1	0.8	8
4west-Cd _{MAC}	0.00162	0.04	15,20,25	15	11	0.05	5	4.3	0.02	0	0	1	0.8	8
4west-Cd _{EQS}	0.000584	0.04	15	15	11	0.05	5	4.3	0.02	0	0	1	0.8	8
4west-Hg _{MAC}	0.00063	0.04	15	15	11	0.05	5	4.3	0.02	0	0	1	0.8	8
4west-Hg _{EQS}	0.00052	0.04	15	15	11	0.05	5	4.3	0.02	0	0	1	0.8	8
Sanitary-Cd _{MAC}	0.025	0.0014	18	15	11	0.04*	5	4.3	0.02	0	0	1	0.2	8
Sanitary-Cd _{EQS}	0.0061	0.0014	18	15	11	0.04*	5	4.3	0.02	0	0	1	0.2	8
Sanitary-Hg _{MAC}	0.000122	0.0014	18	15	11	0.04*	5	4.3	0.02	0	0	1	0.2	8
Sanitary-Hg _{EQS}	0.000061	0.0014	18	15	11	0.04*	5	4.3	0.02	0	0	1	0.2	8
Sanitary-Ni	0.332587	0.0014	18	15	11	0.04*	5	4.3	0.02	0	0	1	0.2	8
Sanitary-Pb	0.025008	0.0014	18	15	11	0.04*	5	4.3	0.02	0	0	1	0.2	8

*For all the cases in Sanitary water CORMIX1 required an ambient velocity lower than 0.05 m/s. Therefore an ambient velocity of 0.04m/s was used in Sanitary water calculations

Appendix 5. Input data of CORMIX3 with the dissolved metal concentrations for year 2010, scenario 3

Scenario 3		Effluent characteristics				Ambient characteristics				Discharge characteristics				
Discharge point	Concentration (mg/l)	Flow rate (m ³ /s)	Temperature (°C)	Average depth (m)	Depth at discharge (m)	Ambient Velocity (m/s)	Ambient Wind speed (m/s)	Temperature (°C)	Darcy friction	Horizontal angle	Bottom slope	Local depth (m)	Pipe diameter (m)	Bottom invert depth (m)
1-Cd _{MAC}	0.00126	0.14	27.5	5	5	0.05	5	4.3	0.02	90	15	3	1	1
1-Cd _{EQS}	0.0006	0.14	27.5	5	5	0.05	5	4.3	0.02	90	15	3	1	1
1-Hg _{MAC}	0.00853	0.14	27.5	5	5	0.05	5	4.3	0.02	90	15	3	1	1
1-Pb	0.0024	0.14	27.5	5	5	0.05	5	4.3	0.02	90	15	3	1	1
2-Cd _{MAC}	0.001386	0.0893	25	5	5	0.05	5	4.3	0.02	90	15	3	0.6	0.6
2-Cd _{EQS}	0.000405	0.0893	25	5	5	0.05	5	4.3	0.02	90	15	3	0.6	0.6
2-Hg _{MAC}	0.000027	0.0893	25	5	5	0.05	5	4.3	0.02	90	15	3	0.6	0.6
3-Cd _{MAC}	0.001433	0.397	25	5	5	0.05	5	4.3	0.02	90	15	3	1	1
3-Cd _{EQS}	0.000522	0.397	25	5	5	0.05	5	4.3	0.02	90	15	3	1	1
3-Hg _{MAC}	0.00068	0.397	25	5	5	0.05	5	4.3	0.02	90	15	3	1	1
3-Hg _{EQS}	0.000313	0.397	25	5	5	0.05	5	4.3	0.02	90	15	3	1	1

Appendix 6. Input data of CORMIX1 with the dissolved metal concentrations for year 2010, scenario 3

Scenario 3		Effluent characteristics				Ambient characteristics				Discharge characteristics				
Discharge point -metals	Discharge concentration (mg/l)	Flow rate (m³/s)	Temperature (°C)	Average depth HA(m)	Depth at discharge HD (m)	Ambient velocity (m/s)	Wind speed (m/s)	Temperature (°C)	Darcy friction coefficient	Horizontal angle	Vertical angle	Distance to the nearest bank (m)	Pipe diameter (m)	Discharge port height H0 (m)
4-Cd _{MAC}	0.001433	1.12	20	5	4	0.05	5	4.3	0.02	0	0	1	0.8	3
4-Cd _{EQS}	0.000685	1.12	20	5	4	0.05	5	4.3	0.02	0	0	1	0.8	3
4-Hg _{MAC}	0.00068	1.12	20	5	4	0.05	5	4.3	0.02	0	0	1	0.8	3
4west-Cd _{MAC}	0.00162	0.04	20	5	4	0.05	5	4.3	0.02	0	0	1	0.8	3
4west-Cd _{EQS}	0.000584	0.04	20	5	4	0.05	5	4.3	0.02	0	0	1	0.8	3
4west-Hg _{MAC}	0.000063	0.04	20	5	4	0.05	5	4.3	0.02	0	0	1	0.8	3
4west-Hg _{MAC}	0.000052	0.04	20	5	4	0.05	5	4.3	0.02	0	0	1	0.8	3
Sanitary-Cd _{MAC}	0.025	0.0014	18	5	4	0.04*	5	4.3	0.02	0	0	1	0.2	3
Sanitary-Cd _{EQS}	0.0061	0.0014	18	5	4	0.04*	5	4.3	0.02	0	0	1	0.2	3
Sanitary-Hg _{MAC}	0.000122	0.0014	18	5	4	0.04*	5	4.3	0.02	0	0	1	0.2	3
Sanitary-Hg _{EQS}	0.000061	0.0014	18	5	4	0.04*	5	4.3	0.02	0	0	1	0.2	3
Sanitary-Ni	0.332587	0.0014	18	5	4	0.04*	5	4.3	0.02	0	0	1	0.2	3
Sanitary-Pb	0.025008	0.0014	18	5	4	0.04*	5	4.3	0.02	0	0	1	0.2	3

*For all the cases in Sanitary water CORMIX1 required an ambient velocity lower than 0.05 m/s. Therefore an ambient velocity of 0.04m/s was used in Sanitary water calculations.

Appendix 7. Input data of CORMIX3 with the dissolved metal concentrations for year 2010, scenario 4

Scenario 4		Effluent characteristics				Ambient characteristics				Discharge characteristics				
Discharge point - metals	Discharge - e concentration (mg/l)	Flow rate (m3/s)	Temperature (°C)	Average depth (m)	Depth at discharge (m)	Ambient velocity (m/s)	Wind speed (m/s)	Temperature (°C)	Darcy friction	Horizontal angle	Bottom slope	Local depth (m)	Pipe diameter (m)	Bottom invert depth (m)
1-Cd _{MAC}	0.00126	0.14	27.5	1	1	0.05	5	4.3	0.02	90	15	1	1	1
1-Cd _{EQS}	0.0006	0.14	27.5	1	1	0.05	5	4.3	0.02	90	15	1	1	1
1-Hg _{MAC}	0.00853	0.14	27.5	1	1	0.05	5	4.3	0.02	90	15	1	1	1
1-Pb	0.0024	0.14	27.5	1	1	0.05	5	4.3	0.02	90	15	1	1	1
2-Cd _{MAC}	0.001386	0.0893	25	0.6	0.6	0.05	5	4.3	0.02	90	15	0.6	0.6	0.6
2-Cd _{EQS}	0.000405	0.0893	25	0.6	0.6	0.05	5	4.3	0.02	90	15	0.6	0.6	0.6
2-Hg _{MAC}	0.000027	0.0893	25	0.6	0.6	0.05	5	4.3	0.02	90	15	0.6	0.6	0.6
3-Cd _{MAC}	0.001433	0.397	25	1	1	0.05	5	4.3	0.02	90	1	1	1	1
3-Cd _{EQS}	0.000522	0.397	25	1	1	0.05	5	4.3	0.02	90	1	1	1	1
3-Hg _{MAC}	0.00068	0.397	25	1	1	0.05	5	4.3	0.02	90	1	1	1	1
3-Hg _{EQS}	0.000313	0.397	25	1	1	0.05	5	4.3	0.02	90	15	1	1	1

Appendix 8. Input data of CORMIX1 with the dissolved metal concentrations for year 2010, scenario 4

Scenario 4		Effluent characteristics				Ambient characteristics				Discharge characteristics				
Discharge point	Discharge concentration (mg/l)	Flow rate (m ³ /s)	Temperature (°C)	Average depth (m)	Discharge depth (m)	Ambient velocity (m/s)	Wind speed (m/s)	Temperature (°C)	Discharge velocity (m/s)	Horizontal angle	Vertical angle	Distance to the nearest bank (m)	Pipe diameter (m)	Discharge height (m)
4-Cd _{MAC}	0.001433	1.12	20	3	3	0.05	5	4.3	0.02	0	0	1	0.8	2.4
4-Cd _{EQS}	0.000685	1.12	20	3	3	0.05	5	4.3	0.02	0	0	1	0.8	2.4
4-Hg _{MAC}	0.00068	1.12	20	3	3	0.05	5	4.3	0.02	0	0	1	0.8	2.4
4west-Cd _{MAC}	0.00162	0.04	20	3	3	0.05	5	4.3	0.02	0	0	1	0.8	2.4
4west-Cd _{EQS}	0.000584	0.04	20	3	3	0.05	5	4.3	0.02	0	0	1	0.8	2.4
4west-Hg _{MAC}	0.000063	0.04	20	3	3	0.05	5	4.3	0.02	0	0	1	0.8	2.4
4west-Hg _{MAC}	0.000052	0.04	20	3	3	0.05	5	4.3	0.02	0	0	1	0.8	2.4
Sanitary-Cd _{MAC}	0.025	0.0014	18	3	3	0.04*	5	4.3	0.02	0	0	1	0.2	2.4
Sanitary-Cd _{EQS}	0.0061	0.0014	18	3	3	0.04*	5	4.3	0.02	0	0	1	0.2	2.4
Sanitary-Hg _{MAC}	0.000122	0.0014	18	3	3	0.04*	5	4.3	0.02	0	0	1	0.2	2.4
Sanitary-Hg _{EQS}	0.000061	0.0014	18	3	3	0.04*	5	4.3	0.02	0	0	1	0.2	2.4
Sanitary-Ni	0.332587	0.0014	18	3	3	0.04*	5	4.3	0.02	0	0	1	0.2	2.4
Sanitary-Pb	0.025008	0.0014	18	3	3	0.04*	5	4.3	0.02	0	0	1	0.2	2.4

Appendix 9. Input data for sensitivity analysis, CORMIX3 with the dissolved metal concentrations for year 2010, point 1-Cd , from scenario 2.

Sensitivity analysis		Effluent characteristics				Ambient characteristics				Discharge characteristics				
Discharge point -metals	Discharge concentration EQS/MAC (mg/l)	Flow rate (m3/s)	Temperature (°C)	Average depth HA(m)	Depth at discharge HD (m)	Ambient velocity (m/s)	Wind speed (m/s)	Temperature (°C)	Darcy friction	Horizontal angle	Bottom slope	Local depth (m)	Piper diameter (m)	Bottom invert depth (m)
Main scenario	0.0006/0.00126	0.14	25	15	15	0.05	5	4.3	0.02	90	15	10	1	1
Flow rate x 2	0.0006/0.00126	0.28	25	15	15	0.05	5	4.3	0.02	90	15	10	1	1
Flow rate /2	0.0006/0.00126	0.07	25	15	15	0.05	5	4.3	0.02	90	15	10	1	1
Effluent temperature +2 °C	0.0006/0.00126	0.14	27	15	15	0.05	5	4.3	0.02	90	15	10	1	1
Effluent temperature -2 °C	0.0006/0.00126	0.14	23	15	15	0.05	5	4.3	0.02	90	15	10	1	1
Average depth +2	0.0006/0.00126	0.14	25	17	15	0.05	5	4.3	0.02	90	15	10	1	1
Average depth -2	0.0006/0.00126	0.14	25	13	15	0.05	5	4.3	0.02	90	15	10	1	1
Ambient velocity x2	0.0006/0.00126	0.14	25	15	15	0.1	5	4.3	0.02	90	15	10	1	1
Ambient velocity /2	0.0006/0.00126	0.14	25	15	15	0.025	5	4.3	0.02	90	15	10	1	1
Ambient temperature +2 °C	0.0006/0.00126	0.14	25	15	15	0.05	5	6.3	0.02	90	15	10	1	1
Ambient temperature -2 °C	0.0006/0.00126	0.14	25	15	15	0.05	5	2.3	0.02	90	15	10	1	1

Appendix 10. Input data for sensitivity analysis, CORMIXI with the dissolved metal concentrations for year 2010, point 4-Cd, from scenario 2.

Scenario 1	Effluent characteristics				Ambient characteristics				Discharge characteristics					
Discharge point -metals	Discharge concentration ,EQS/MAC (mg/l)	Flow rate (m3/s)	Tem perature (°C)	Average depth HA(m)	Depth at dischar -ge HD (m)	Amb- ient Velo- city (m/s)	Wind speed (m/s)	Tempe -rature (°C)	Darcy fricti- on	Hori zo- ntal angle	Verti- cal angle	Distanc e to the nearest bank (m)	Pipe diamet- er (m)	Discha -rge port height (m)
Main scenario	0.000685/0.00162	1.12	15	15	11	0.05	5	4.3	0.02	0	0	1	0.8	8
Flow rate x 2	0.000685/0.00162	2.24	15	15	11	0.05	5	4.3	0.02	0	0	1	0.8	8
Flow rate /2	0.000685/0.00162	0.56	15	15	11	0.05	5	4.3	0.02	0	0	1	0.8	8
Effluent temperature +2 °C	0.000685/0.00162	1.12	13	15	11	0.05	5	4.3	0.02	0	0	1	0.8	8
Effluent temperature -2 °C	0.00068/0.00162	1.12	17	15	11	0.05	5	4.3	0.02	0	0	1	0.8	8
Average depth +2	0.000685/0.00162	1.12	15	17	11	0.05	5	4.3	0.02	0	0	1	0.8	8
Average depth -2	0.000685/0.00162	1.12	15	13	11	0.05	5	4.3	0.02	0	0	1	0.8	8
Ambient velocity x2	0.000685/0.00162	1.12	15	15	11	0.1	5	4.3	0.02	0	0	1	0.8	8
Ambient velocity /2	0.000685/0.00162	1.12	15	15	11	0.025	5	4.3	0.02	0	0	1	0.8	8
Ambient temperature +2 °C	0.000685/0.00162	1.12	15	15	11	0.05	5	6.3	0.02	0	0	1	0.8	8
Ambient temperature -2 °C	0.000685/0.00162	1.12	15	15	11	0.05	5	2.3	0.02	0	0	1	0.8	8

Appendix I.1. Input data of CORMIX3 with the dissolved metal concentrations for year 2010, mixing zone overlapping case

Scenario I	Effluent characteristics			Ambient characteristics				Discharge characteristics							
	Discharge point	Discharge- concentra- tion	Flow rate (m ³ /s)	Tempera- ture (°C)	Average depth HA(m)	Depth at discharge HD (m)	Ambie nt velocit y (m/s)	Wind speed (m/s)	Temperat -ure (°C)	Darc -y fricti on	Horizo -ntal angle	Bottom slope	Local depth (m)	Pipe diamet- er (m)	Bottom invert depth (m)
	3-Cd _{EQS}	0.0005	0.49	25	15	15	0.05	5	4.3	0.02	90	15	10	1	1
	3-Cd _{MAC}	0.00143	0.49	25	15	15	0.05	5	4.3	0.02	90	15	10	1	1
	3-Hg _{MAC}	0.000677	0.49	25	15	15	0.05	5	4.3	0.02	90	15	10	1	1

Appendix 12. Example of the visual dilution and mixing zone based on Cd concentration of point 4, at temperature 15°C

