

CHEMICAL SAFETY REPORT

Sections 9 and 10

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Legal name of applicant:	Società Chimica Bussi S.p.A.
Submitted by:	Società Chimica Bussi S.p.A.
Substance:	Sodium Dichromate (EC Number: 234-190-3; CAS Number: 10588-01-9 / 7789-12-0)
Use title:	Use of SD as an additive for suppressing parasitic reactions and oxygen evolution, pH buffering and cathode corrosion protection in the electrolytic manufacture of sodium chlorite.
Use number:	1

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Table of Contents

Table of Contents.....	ii
9. EXPOSURE ASSESSMENT (and related risk characterisation).....	1
9.0 Introduction	1
9.0.1. Overview of uses and Exposure Scenarios	1
9.0.2. Introduction to the assessment.....	4
9.0.2.1. Environment	4
9.0.2.2. Man via environment.....	5
9.0.2.3. Workers	10
9.0.2.4. Consumers	77
9.0.3. Exposure-risk relationships (ERRs) for carcinogenic effects and DNEL values for reproductive toxicity used for the assessment.....	77
9.1. Exposure scenario 1: Use at industrial site - Use of SD as an additive for suppressing parasitic reactions and oxygen evolution, pH buffering and cathode corrosion protection in the electrolytic manufacture of sodium chlorite.....	79
9.1.1. Environmental contributing scenario 1	80
Exposure and risks for the environment and man via the environment	81
9.1.2. Worker contributing scenario 1: T1: Feeding SD solution into the process (PROC 8b)	86
9.1.2.1. Conditions of use	86
9.1.2.2. Exposure for workers.....	86
9.1.3. Worker contributing scenario 2: T2: Use in closed batch process: Sampling of the electrolyte solution (PROC 3).....	88
9.1.3.1. Conditions of use	88
9.1.3.2. Exposure and risks for workers	89
9.1.4. Worker contributing scenario 3: T3: Production lab analyses (PROC 15)	92
9.1.4.1. Conditions of use	92
9.1.4.2. Exposure and risks for workers	93
9.1.5. Worker contributing scenario 4: T4: Maintenance and cleaning (PROC 8a)	95
9.1.5.1. Conditions of use	95
9.1.5.2. Exposure and risks for workers	96
9.1.6. Aggregated exposure estimation and risk characterisation for unit operators	99
9.1.6.1 Exposure estimation.....	99
9.1.6.2 Risk characterisation.....	104
9.1.7. Worker contributing scenario 5: T5: Central lab analyses (PROC 15).....	104
9.1.7.1. Conditions of use	104
9.1.7.2. Exposure estimation.....	105
9.1.7.2 Risk characterisation.....	106
9.2 Dermal exposure.....	107
9.2.1 Conditions of use (Riskofderm modelling, realistic input, for details see Annex 8)	107

10. RISK CHARACTERISATION RELATED TO COMBINED EXPOSURE	111
10.0 Human health – Qualitative Risk Characterisation of acute dermal and inhalation toxic effects and local effects on skin, eyes and respiratory tract at the workplace.....	111
10.1. Human health.....	112
10.1.1. Workers	112
10.1.2. Consumer.....	112
10.2. Environment (combined for all emission sources)	112
10.2.1. All uses (regional scale).....	113
10.2.2. Local exposure due to all wide dispersive uses	113
10.2.3. Local exposure due to combined uses at a site	113
Annex 1 Extract of GESTIS database International limit values for chemical agents Occupational exposure limits (OELs)	114
Annex 2 Air monitoring report (extracts).....	115
Annex 3A Statistical evaluation of air monitoring data.....	118
Annex 3B Monitoring data from Caffaro Brescia (CB)	122
Annex 3C Site specific data for Società Chimica Bussi S.p.A. (SCB).....	124
Annex 4 Photo documentation	127
Annex 5 ART modelling input and results.....	135
Annex 6 Survey data	141
Annex 7 Chromium measurements final product of Caffaro Brescia.....	142
Annex 8 Riskofderm modelling and results	143
References	144

List of Tables

Table 1. Overview of exposure scenarios and contributing scenarios	4
Table 2. Derived release factors for releases to wastewater	8
Table 3. Input data for sodium dichromate in EUSES modelling	9
Table 4. Type of risk characterisation required for workers	10
Table 5. Task definition	14
Table 6. Critical input parameters (bold print indicates values used in modelling)	74
Table 7. Exposure-risk relationships for inhalation exposure of workers used for calculating risks due to SD exposure (from ECHA, 2013)	77
Table 8. Exposure-risk relationships for inhalation exposure of general population used for calculating risks due to SD exposure (from ECHA, 2013)	77
Table 9. Exposure-risk relationships for oral exposure of general population used for calculating risks due to SD exposure of humans via environment (from ECHA, 2013)	78
Table 10. Summary of air monitoring results	79
Table 11. Local releases to the environment	80
Table 12. Modelled exposure for humans via the environment: inhalation	81
Table 13. Modelled exposure for humans via the environment: oral (drinking water and fish)	82
Table 14. Risk estimates for humans via the environment (general population, local assessment)	83
Table 15. Risk estimates for humans via the environment (general population, regional assessment)	83
Table 16. RCRs for humans via the environment	85
Table 17. Monitored exposure for workers: task 1	87
Table 18. Modelled Exposure for Workers: task 1	87
Table 19. Monitored exposure for workers: task 2	90
Table 20. Modelled exposure for workers: task 2	91
Table 21. Monitored exposure for workers: task 3	93
Table 22. Modelled exposure for workers: task 3	94
Table 23. Monitored exposure for workers: task 4 (cleaning)	96
Table 24. Modelled exposure for workers: task 4 (maintenance)	97
Table 25. Shift patterns for aggregated exposure estimation	99
Table 26. Workers engaged in sodium chlorite production at the SCB site in Bussi sul Tirino.	100
Table 27. Task-specific and aggregated long-term TWA inhalation exposure estimates for unit operators and mechanical day workers	101
Table 28. Risk resulting from Cr(VI) exposure during its industrial use as a process chemical in sodium chlorite production	104
Table 29. Modelled exposure for workers: task 5	105
Table 30. Risk resulting from Cr(VI) exposure during its industrial use as a process chemical in sodium chlorate or chlorite production: lab staff (task 5)	106
Table 31. Modelled Exposure for Workers: T2 (hands), T3 (hands), and T5 (hands) based on Riskofderm	108
Table 32. Modelled Exposure for Workers for all tasks based on a default dermal load of 0.1 mg/cm ² /d (generic approach)	108
Table 33. Exposure concentrations and risks for workers (dermal exposure)	110
Table 34. Combined RCRs resulting from Cr(VI) exposure during its industrial use as a process chemical in sodium chlorite production	110
Table 35: Air monitoring data from Caffaro Brescia used in former AfA	122
Table 36: Air monitoring data from Caffaro Brescia generated since former AfA	122
Table 37: Monitoring data for waste water after Cr(VI) reduction from Caffaro Brescia generated since former AfA	122
Table 38: Flow rates for rivers Pescara, Tirino and combined flow after junction immediately downstream of SCB waste water influent site: 2006 to 2013	125

List of Figures

Figure 1 Correlation between dust and Cr(VI) concentrations for task 2 (sampling)	91
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9. EXPOSURE ASSESSMENT (and related risk characterisation)

9.0 Introduction

This application for authorisation (AfA) is for the new sodium chlorite production plant of Società Chimica Bussi S.p.A. (called SCB in the following) which shall be constructed at the industrial site in Bussi. As the plant is not operative yet there are no plant specific monitoring values available for this future use at the Bussi site. However, the whole process follows a technology which is described by the Reference Document on Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals - Solids and Others industry (EC, 2007) and which is very similar for all companies which produce sodium chlorate, which is an important precursor of sodium chlorite. Especially, the future plant of SCB will in principle be comparable to the sodium chlorite plant of Caffaro Brescia (called CB in the following), which like SCB belongs to the same owner, and for which an authorisation for the same use as applied for in this AfA has been granted in the past¹. As the future SCB plant will apply a very similar technology as CB this AfA is based on the exposure assessment used by CB and the whole group of sodium chlorate producing companies. This means, that the monitoring values, which were collected in the former AfA process for the different sodium chlorate producers as well as the exposure modelings form the basis for the exposure assessment presented here. Where applicable, modulations of the exposure assessment have been performed to consider the relevant parameters (e.g. duration, frequency, SD concentration) of the future SCB plant. Especially, differences to the former exposure assessment which are due to technological improvements or organisational changes in the work procedure are highlighted and their influence on the overall exposure assessment is discussed.

9.0.1. Overview of uses and Exposure Scenarios

‘Sodium dichromate (SD) is used as a processing aid in the production of sodium chlorite in an industrial setting.

Sodium chlorite is a substance/ intermediate that is primarily used in the treatment of potable, industrial and waste water for both biocidal and non-biocidal purposes where it is/can be converted into chlorine dioxide. Additionally, it is used in pulp and paper production where it is converted into chlorine dioxide, which in turn is used as a bleaching agent (EC, 2007) and in other industrial sectors. Sodium chlorite is produced in several steps, with the first step being production of sodium chlorate and the second step conversion of sodium chlorate to chlorine gas and chlorine dioxide by the addition of hydrochloric acid. The two gases are separated by exploiting their different solubility and Chlorine dioxide is then adsorbed to sodium hydroxide and hydrogen peroxide under formation of sodium chlorite, the transportation form of chlorine dioxide.

Sodium chlorate is produced by electrolysis of sodium chloride brine, yielding hydrogen gas a co-product. Electrolysis of sodium chloride (brine) is performed under pH conditions where the chlorine from the anode remains combined with sodium hydroxide in the form of sodium hypochlorite, which is then converted into sodium chlorate and chloride. Sodium dichromate acts to increase the current efficiency by suppressing parasitic cathodic reactions, and thus to avoid cathodic reduction of hypochlorite and chlorate. It also has a number of other beneficial roles in that it acts as a pH buffer and reduces anodic oxygen generation. Inhibition of this side-reaction is an important part of the process, both for current efficiency and safety concerns due to the potential

¹ COMMISSION IMPLEMENTING DECISION of 7.6.2017 granting an authorisation for a use of sodium dichromate under Regulation (EC) No 1907/2006 of the European Parliament and of the Council (Caffaro Brescia S.r.l.). see https://echa.europa.eu/de/applications-for-authorisation-previous-consultations/-/substance-rev/12463/term?_viewsubstances_WAR_echarevsubstanceportlet_SEARCH_CRITERIA_EC_NUMBER=234-190-3&_viewsubstances_WAR_echarevsubstanceportlet_DISS=true

explosive atmospheres formed in presence of hydrogen. During the second step, formation of chlorine dioxide and chlorine gas from sodium chlorate in the presence of hydrochloric acid in the reactor the presence of sodium dichromate also increases the efficiency of the process. It suppresses parasitic reactions which would negatively affect the yield.

The process can briefly be summarised as following: Sodium chloride/sodium chlorate brine, from the sodium chlorite plant is transported to the electrolysis cells where it is transformed electrochemically, in the presence of sodium dichromate, to sodium hypochlorite which in turn is converted into sodium chlorate. The resulting solution, rich in sodium chlorate and with a lower content of chloride, is fed in the “chlorine dioxide generator” (a closed reactor working under mild vacuum). By addition of a 32% hydrochloric acid (HCl) solution [REDACTED] with step-wise elevation of temperature [REDACTED] chlorine dioxide (ClO₂) and chlorine (Cl₂) gas are formed. The ClO₂ generator is a horizontal cylindrical titanium vessel [REDACTED]. An excess of chilled strong chlorate solution is mixed with hydrochloric acid [REDACTED]. Dilution air is sparged into each compartment below the liquor surface to i) improve mixing and ii) keep ClO₂ concentration at the optimum level [REDACTED]. The gaseous flow from the generator is a mixture of ClO₂, Cl₂, water vapour and air. It is fed into the ClO₂ absorption column, where the ClO₂ plus some of the chlorine are absorbed in chilled water [REDACTED] to produce a chlorine dioxide solution [REDACTED]. The gas from the absorber leaving the column at the top (mainly Cl₂ and air) is partly recycled to the generator to dilute the ClO₂, and partly sent to the HCl plant on-site. The ClO₂ solution is sent to the chlorine dioxide desorption tower to generate pure ClO₂ gas. The flow from the desorption tower [REDACTED] is sent to two columns arranged in series where chlorine dioxide is adsorbed by hydrogen peroxide and caustic soda solution under formation of sodium chlorite.

Sodium dichromate quantitatively remains in the reaction liquor (weak chlorate brine) inside the chlorine dioxide generation reactor. Excess water formed during the process is evaporated via a new weak chlorate evaporator directly coupled with the ClO₂ generator. As a consequence, SD concentration is kept essentially constant throughout the whole process, i.e. during chlorate formation by electrolysis as well as in the weak chlorate brine after ClO₂ formation, SD concentration is at max. 5 g/L (ca. 0.4% by weight). Weak chlorate brine is then transferred back to the sodium chlorate production unit.

The process is carried out in a closed loop system with very small quantities of sodium dichromate used per tonne of sodium chlorate produced (10-150 g SD/t sodium chlorate; EC, 2007). The only losses of chromium from the process are due to periodic maintenance and sampling or due to losses of chromium as impurity of the final product and in waste sludges generated in the process. Overall, the system is characterised by a high degree of closure from an environmental perspective as well as substantial recirculation of SD. Due to the electrochemical nature of the process, part of the Cr(VI) from SD is reduced to Cr(III) in the process (see EC (2007)). ‘As a principal risk management measure, SD is purchased as a liquid solution in water (rather than in its pure solid form) with a maximum concentration of 70% SD. The substance is rapidly diluted to concentrations well below 1% in the electrolyte solution (maximum 0.464%; see section “critical input parameters” in section 9.0.2.3 below for details on SD and Cr(VI) concentrations).

Technical innovations introduced into the new SCB site

The following technical improvements, which will be introduced at the SCB Bussi site (“Site E”) will improve (reduce) the exposure of workers as well as the environment:

- New and much more efficient electrolysis cells will be installed at SCB site. [REDACTED] This leads to a lower probability for leakages.
- The new cells will be installed in an open hall (under canopy) ensuring excellent ventilation, reducing further the possibility of inhalation exposure for workers. Old figures for air concentrations based on factory volume will therefore be conservative if used for new factory.
- The site will be built [REDACTED] to prevent any leakage to the surrounding area in case of any accidental release.
- Excess water formed during the process is evaporated via a new weak chlorate evaporator directly coupled with the ClO₂ generator. As a consequence, SD concentration is kept essentially constant throughout the whole process, i.e. during chlorate formation by electrolysis as well as in the weak chlorate brine after ClO₂ formation, SD concentration is at max. 5 g/L (ca. 0.4% by weight). In consequence, workers’ risk for exposure during sampling is considerably lower because of
 - Generally lower SD concentration compared to CB in AfA 2015 (6.5 g/L in chlorate rich solution);
 - No sampling step existing anymore associated with high SD concentration – at CB in AfA


2015, high SD concentration of 29 g/L of weak chlorate brine sampled during NaClO₂ production.

- Consequently no laboratory analysis of the high SD concentration solution necessary. This results in the deletion of two worker contributing scenarios of the former CB AfA, i.e. sampling during the sodium chlorite production and laboratory analysis of these samples with an increased SC concentration.
- The [REDACTED] water evaporated is just in the amount of excess water formed during reaction processes. This contributes to the consistently low SD concentration throughout the production process of ca. 0.4% by weight. At CB (AfA 2015) ClO₂ generator works under high vacuum, leading to i) a high loss of water, ii) oversaturation of the weak chlorate solution, and thus iii) high SD concentration (see above).
- Evaporation in the weak chlorate evaporator at SCB proceeds under very mild conditions preventing formation of aerosols which theoretically could lead to a loss of SD to the water condensate. Evaporated water at SCB together with water abstracted during ClO₂ generation is re-used by [REDACTED] % for on-site HCl production (HCl used quantitatively within the ClO₂ generation process). Only ca. [REDACTED] % of the condensed water is sent to waste water (reductively treated), while at CB (AfA 2015) this water could not be re-used. Non-condensed vapour including some chlorine is transferred to the absorber.
- Before strong chlorate liquor enters the ClO₂ generator it must be filtered to remove any solid particles [REDACTED]. At CB this was done using a filter press (former task 5) which had to be cleaned manually by workers at regular intervals. Instead of the filter press, SCB site will be equipped with a pair of ceramic candle filters, one in use and one for switching in case of cleaning. [REDACTED] For cleaning, the flow is switched to the spare filter and the one destined for cleaning is disconnected. The chlorate liquor containing SD is drained from the filter to the strong chlorate feed tank. The filter is filled with water and cleaned via backwash ("hydroshocking") using air pressure waves. After washing, a sufficient settling time as well as the suction of the air phase of the receiver towards the washing towers will ensure that any exposure of workers from spray / aerosol is avoided. The waste water (containing particulates) will not enter the waste water reduction system but will be collected and sent to an authorized hazardous waste treatment outside the factory. In consequence, this new filter system
 - Will reduce worker's exposure to the absolute minimum possible;
 - In fact one worker contributing scenario (former task 5: filter press) is no longer applicable and could be deleted for this AfA;
 - Will reduce environmental exposure considerably (low volume of hazardous waste treated outside of the factory, not entering the waste water reduction system and finally the river);
 - Will reduce the overall loss of SD considerably: at maximum 4 washing operations per year with a loss of ca. [REDACTED] per wash will lead to a total loss of [REDACTED] SD per year. As a conservative estimate, a loss of [REDACTED] per year via candle filter cleaning is assumed.
- Due to use of hydrogen chloride (HCl) produced by SCB itself in a highly pure quality (synthesis process and demi-water are used, see above), no impurities from externally provided HCl need to be accounted for as is the case at CB site. This leads to lower amount of impurities on the candle filter and consequently to a low cleaning frequency of the filter (see above).

Tonnage information is contained in other parts of the application for authorisation (AoA, SEA).

The following table lists all the exposure scenarios (ES) assessed in this CSR. The entire process can best be described by the descriptor PROC 3. For the individual tasks identified as potentially being associated with some exposure, additional descriptors were selected (see Table 1). These PROCs primarily serve for orientation but are not key in the exposure assessment performed here, since the monitoring data used in the exposure assessment as well as ART (Advanced Reach Tool) modelling performed in addition are completely independent of PROCs. A detailed description of the tasks performed by workers, the rationale for PROC assignment as well as details on the approach to exposure estimation is given in section 9.0.2.3.

Table 1. Overview of exposure scenarios and contributing scenarios

Identifiers	Market Sector	Titles of exposure scenarios and the related contributing scenarios	Tonnage (tonnes per year)
ES1 - IW1		Use of SD as an additive for suppressing parasitic reactions and oxygen evolution, pH buffering and cathode corrosion protection in the electrolytic manufacture of sodium chlorite. - Industrial use of processing aids (ERC 4) - T1: Feeding SD solution into the process (PROC 8b) - T2: Use in closed batch process: Sampling of the electrolyte solution (PROC 3) - T3: Production lab analyses (PROC 15) - T4: Maintenance and cleaning (PROC 8a) - T5: Central lab analyses (PROC 15)	 (range: 100 kg – 2 tonnes)
Manufacture: M-#, Formulation: F-#, Industrial end use at site: IW-#, Professional end use: PW-#, Consumer end use: C-#, Service life (by workers in industrial site): SL-IW-#, Service life (by professional workers): SL-PW-#, Service life (by consumers): SL-C-#.			

As the final product does not contain any relevant amount of chromium (below 1.1 ppm; see Annex 7) the handling of the final product does not need to be considered in this report.

9.0.2. Introduction to the assessment

As outlined above the overall exposure assessment as presented here was elaborated during the 2015 AfA for a consortium of companies which produce sodium chlorate in Europe with or without subsequent production of chlorine dioxide or sodium chlorite. The manufacturing process of sodium chlorate is comparable for all sites of all companies. Therefore, one general exposure scenario for the sodium chlorate production was developed for all companies to be used in their application for authorisation and which also covers the situation of this applicant except to the differences outlined above. This applicant (SCB) intends to introduce some technical innovations which will improve the process and very likely will reduce environmental exposure (see section 9.0.1 above for details). Therefore, this assessment is essentially identical to the one performed for CB in 2015. However, where technical improvements do result in significant deviations from the previous assessment, this will be explained in added paragraphs relating specifically to the SCB plant. Because the SCB plant is not yet working, release fractions for water are calculated from data for CB plant and applied to SCB, which is considered to be conservative due to the improvements introduced in SCB as well as the high background for chromium in ground water used as industrial water by CB. Accordingly, the exposure of humans via the environment (HvE) is calculated based on the release fraction (RF) to air as derived generally for the consortium of companies in 2015, the RF to waste water derived for CB plant from measured data, as well as the waste water flow for SCB calculated from technical specifications and the river flow rate documented specifically for the SCB site. In consequence, the assumptions and calculations for SCB are introduced under the heading “Site E” in addition to sites A to D already included in the 2015 AfA.

9.0.2.1. Environment

Scope and type of assessment

No environmental assessment is performed because:

- 1) the effects of SD on organisms in the environment did not form the basis of its identification as a substance of very high concern,
- 2) Cr(VI) from SD is expected to be reduced to Cr(III) under most environmental conditions, limiting any potential impact of Cr(VI) to the immediate vicinity of the source (ECB, 2005),

3) sodium chlorite production is characterised by a high degree of closure from an environmental perspective (EC, 2007).

9.0.2.2. Man via environment

Scope and type of assessment

Human SD exposure via the environment due to emissions from the sites covered in this CSR to wastewater streams is considered in section 9.1.1. While no direct emissions to air occur, indirect emissions to air are assessed as described below. In relation to oral exposure of humans via the environment, it has to be acknowledged that Cr(VI) is rapidly reduced to Cr(III) in many environmental compartments. An exposure to Cr(VI) estimated on the basis of releases of Cr(VI) into environmental compartments may therefore significantly overestimate exposure of humans via the environment. In addition, many of the environmental modelling parameters (and partition coefficients in particular) rely on the log K_{ow} of a given substance. This parameter is irrelevant for inorganic substances such as Cr(VI) and the calculated partition coefficients are not applicable.

In addition, there are only few data which report the presence of Cr(VI) in foodstuff (EFSA, 2014). Mostly, only total chromium was determined. Some scarce studies reported that the fraction of Cr(VI) of total chromium is generally below 10% (range 1.31-12.9%). Additionally, some investigations even indicate that there is no Cr(VI) in foodstuff of plant origin at all and that measurement on Cr(VI) are analytical artefacts. This might also be the case in foodstuff of animal origin. Based on these data, the EFSA CONTAM Panel noted 'that there is a lack of data on the presence of Cr(VI) in food, and decided to consider all the reported analytical results in food as Cr(III)'. The CONTAM Panel concluded that it can be considered 'that all the chromium ingested via food is in the trivalent form, in contrast to drinking water where chromium may easily be present in the hexavalent state', primarily due to the use of strong oxidants in drinking water purification (EFSA, 2014). These considerations of the CONTAM Panel strengthen the former evaluation of the EU Risk Assessment Report for chromates, which assessed indirect oral exposure of humans via the environment only for exposure via (drinking) water and fish (ECB, 2005). This approach is also followed here.

The assessment is focused on the carcinogenicity of SD as the most relevant endpoint and compares the exposure estimates with the exposure-risk relationship derived by RAC as described in section 5.11.

Comments on assessment approach:

This section describes the approach to exposure estimation for humans via the environment resulting from the industrial use of SD covered in this CSR. SD is handled in closed-loop processes that show a high degree of closure from an environmental perspective (EC, 2007). Therefore, emissions to the environment are expected to be low. Nonetheless, exposure via ambient air and from oral exposure (through ingestion of drinking water and consumption of fish) were assessed both for the regional and local scale. As there are currently only 12 sites in Europe (13 sites after the SCB plant becomes operative; for further discussion see the SEA document) which use SD for sodium chlorate production and as there is no wide dispersive use of SD the regional assessment is regarded as not relevant in this context, but it is provided for the sake of completeness. EUSES software (v. 2.12) was used for that purpose, since direct use of monitoring data was inappropriate for reasons outlined below.

Monitoring data

Air

Based on the exposure-risk relationship derived by ECHA (2013) for inhalation exposure of the general population a DMEL of 0.0345 ng/m³ associated with an extra risk of 1 x 10⁻⁶ was derived). While such a concentration may theoretically be measured with current sampling and analytical methods (i.e. based on blind values of instruments), experience with real samples suggest that the true limit of detection for Cr(VI) in ambient air samples is considerably higher, e.g. 0.45 ng/m³ (Gladtko et al., 2012).

As a consequence of these considerations and due to the observation that the ambient air concentrations measured at the site premises during the monitoring campaign were all below the LoQ (2.4 ng/m³), additional ambient air monitoring around the sites was not performed. Direct emissions to air are also not expected to occur during the use of SD described here due to the extremely low fugacity of SD dissolved in the electrolyte

solution at very low concentrations. However, the stationary monitoring data for workers described below show some releases to workroom air, resulting in detectable concentrations of Cr(VI) in the immediate vicinity of the source during specific tasks in some cases. In order to analyse whether these Cr(VI) concentrations result in relevant Cr(VI) concentrations for human exposure via the environment, a release factor was derived and used as an input in EUSES modelling of human exposure via ambient air as described below.

Water

Monitoring data for chromium concentrations in the effluent were available for most sites of the companies which produce sodium chlorate as well as for this company (CB), since these are required under national legislation. When these data were analysed for use in the assessment of human exposure via the environment, it turned out that measurements at most sites are performed for total chromium with no differentiation between Cr(III) and Cr(VI). This is due to the fact that national legislation limits the release on the basis of total chromium and compliance has therefore to be shown by measuring total chromium in the effluent.

However, the information retrieved identified measurements from 4 sites that are specific for Cr(VI), with data from 3 sites being adequate to calculate release factors for wastewater during the use of SD covered by this CSR (data from the fourth site will be used as supporting information). For this 2019 AfA, recent data for the years 2016 to 2018 for CB (specific for Cr(VI)) will be presented in addition and used to derive a specific release factor to waste water for the very similar SCB plant (see explanations above). All these data will be presented in more details in the next section.

Modelling exposure of humans via the environment

As indicated above, release factors for emissions to air and wastewater are derived on the basis of monitoring data. The following sections describe the rationale of the approach and the input data used in EUSES modelling.

Releases to air

Since SD is used at low concentrations dissolved in the electrolyte solution, no direct emissions to air occur. The monitoring campaign designed to estimate workers exposure to Cr(VI) identified concentrations of up to 136 ng/m³ close to sources of exposure (see section 9.1 below for details). With the air volume filtered during the 8 h of the monitoring (180.8 m³) and by extending this measurement to the entire day, 136 ng/m³ x 180.8 m³ x 24 h/d / 8 h / 1,000,000,000,000 ng/kg = 7.38⁻⁸ kg/d are expected to be emitted from this source. Of course, there are other sources potentially emitting Cr(VI) in the unit, but the occupational monitoring campaign showed that more than half of all values were below the limit of quantification. For a very conservative indicative assessment and acknowledging the very indirect nature of this approach, we assume that 50 such emission sources exist at one chlorate unit, all leading to the maximum of the monitoring values of 136 ng/m³. These assumptions are clearly a worst case given that more than half of the workroom samples were below the limit of quantification. Further, data specific for the CB site and representative for the applicant's site (SCB) in a conservative way indicate considerably lower exposure: measurements performed between (including) 2012 and 2017 at/during different critical points/tasks all resulted in concentrations below the limit of detection of the method (between 0.3 and 0.4 ng/m³). For details, see Table 35 and Table 36 in Annex 3B.

Based on the outlined conservative assumptions, the total release per unit then becomes 50 x 7.38 x 10⁻⁸ kg/d are = 3.69 x 10⁻⁶ kg/d. An alternative calculation under the assumption that one half of the limit of quantification of the occupational monitoring campaign (i.e. 1.2 ng/m³) is constantly present in the workroom (with a high volume of 130 000 m³/d assumed) results in a 23-times lower value of 1.56 x 10⁻⁷ kg/d. With a median workroom size of 1 000 m³ (see **Table 6** below), this volume includes 130 air changes per day or 5 air changes per hour.

In order to obtain a maximum release factor, a low amount of SD consumed per site per day of 5 kg/d (2 kg Cr(VI)/d) was used based on survey data. The resulting release factor air for this indicative estimate is 3.69 x 10⁻⁶ kg/d / 2 kg/d = 1.84 x 10⁻⁶.

In addition, dust of sodium chlorate may be emitted to air during drying of sodium chlorate crystals. This step, however, is formally excluded due to the low Cr(VI) concentration in sodium chlorate (see section 9.0.1). We nonetheless included this potential pathway in the assessment of human exposure via the environment. The release factor is calculated from the following data reported in the IPPC reference document (EC, 2007):

- Maximum amount of SD used for production of 1 tonne of sodium chlorate: 150 g/t, corresponding to 59.55 g Cr(VI)/t

- Maximum emission of sodium chlorate dust air for production of 1 tonne of sodium chlorate: 10 g/t

The mean of all maximum amounts of Cr(VI) in the final product (sodium chlorate) reported by the companies which produce sodium chlorate is 5.6 ppm (5.6 µg/g, see Annex 6). Under the assumption that the Cr(VI) concentration in the chlorate dust is similar to the one in sodium chlorate, the amount of Cr(VI) in dust emitted can be approximated to (10 g dust/t sodium chlorate x 5.6 µg Cr(VI)/g dust =) 56 µg/t sodium chlorate produced. The release factor is $56 \mu\text{g}/59.55 \text{ g} = 0.94 \times 10^{-6}$. A lower figure of 0.42×10^{-6} is obtained if the minimum values of the chlorate-normalised values for SD consumption and dust emission from the IPPC reference document (EC, 2007) are used.

The sum of these two release factors (1.84×10^{-6} and 0.94×10^{-6}) for indirect emissions to air of 2.78×10^{-6} is used in the assessment of human exposure via the environment. While it suggests very low releases of Cr(VI) to air, it is based on maximum values of monitoring data for both pathways (maximum of air monitoring, mean of all maximum values for Cr(VI) concentration in dust) as well as a maximum value for dust emissions. It is therefore considered to represent a worst case situation unlikely to exist in reality.

A release factor of 2.78×10^{-6} is used for releases to air in modelling human exposure via the environment. It has to be reiterated that this represents a worst case value for an indicative assessment for a pathway impossible to analyse by other means.

For this AfA (SCB site) this general approach represents an unrealistic worst case as no drying of sodium chlorate takes place in their process. Because of this, the exposure estimation for SCB (termed “site E” below) is performed using the release factor to air of 1.84×10^{-6} , i.e. the release factor for their company will be only about 2/3 of the value used in case of sites A to C for the following calculations.

Releases to wastewater

Site-specific information from 3 sites (A-C, supporting information from site D) was used to derive a release factor for emissions to wastewater. Additionally, for this AfA, very recent (2016 to 2018) site-specific information from CB is used to estimate the release factor to waste water for SCB in a conservative way. As outlined above, the derived release factors (sites A to C and site E, respectively) are based on site-specific measurements of Cr(VI) in the STP or waste water effluent. Concentrations of Cr(VI) were used rather than total Cr concentrations, since the latter are less specific. The fraction of Cr(VI) out of total Cr at these sites ranges between about 6-70%. The differences between the sites are most probably not related to the use covered by this CSR, but are more likely to reflect differences in background Cr concentrations. Total Cr concentrations are known to vary largely with the geochemical conditions. The FOREGS-EuroGeoSurveys Geochemical Baseline Database² reports total Cr concentrations in stream waters across Europe between 0.0050-43 µg/L (n=804, AM: 0.79 µg/L, Median: 0.38 µg/L). Especially the wells used for the retrieval of industrial water of CB have chromium concentrations covering the upper end (mean values in the range of 15.71-35.25 µg/L). In comparison, total chromium in river water used as industrial water at the site of the applicant of this AfA (SCB) is below the quantification limit of the method applied (LoQ: 25 µg/L)³.

Releases to wastewater were calculated for the sites from measured Cr(VI) concentrations in the STP effluent (in ng/L) or waste water effluent, in case where no biological STP was in place (Site B and Site E = SCB - applicant). These measurements were generally performed according to accepted international or national standards (e.g. ISO 18412 and ISO 11083). The measured Cr(VI) concentrations were multiplied by the site-specific STP discharge rate (in m³/d). This release (in kg/d) was then divided by the amount of Cr(VI) used per day at each site. Since the site-specific data constitute confidential information, the exact site-specific values are not shown here. Rather, the calculated releases are summarised in the following table.

Site D was included here for comparison only. This site operates a batch reduction of the wastewater prior to direct discharges. The dataset also contains a few high values. These represent cases, where the reduction was not as efficient as calculated. Additional reduction was then performed prior to discharge. The values account for the comparatively high maximum for site D in the following table. The mean values, however, show the lower release of Cr(VI) due to reduction.

Further, new data for waste water from the CB site are available (2016 to 2018; measured on a quarterly basis), regarded as a representative worst case for the applicant's site (Site E, i.e. SCB) due to the high chromium

² <http://weppi.gtk.fi/publ/foregsatlas/ForegsData.php>

³ Analytical data can be provided by the applicant if requested by ECHA.

background values found at Caffaro Brescia (CB) for industrial water (ground water). Both, the CB site as well as the SCB operate a continuous reduction of waste water exiting the chlorite plant. The system consists of tanks for reduction and neutralization. Tank size is ca. 20 m³ and reduction with sodium metabisulfite (Na₂S₂O₅) occurs under agitation with a contact time of ca. 30 minutes (absolute minimum: 15 minutes). Oxidized chlorinated species as well as Cr(VI) is reduced. The redox potential is continually monitored and reduction is practically quantitative (in presence of excess sodium metabisulfite, the redox potential falls below 400 mV). Before release, pH of waste water is adjusted to pH of ca. 7 (on line) and Cr(VI) will be measured at SCB once a working day (Mo to Fr) before release into the river. In the table below is a summary of the data used for Site E – all values for Cr(VI) were below the limit of quantification. For details on measurements please see **Table 37** in Annex 3B.

Table 2. Derived release factors for releases to wastewater

	Site A	Site B	Site C	Range	Site D*	Site E*
No. of samples	250	25**	1090		250	12
Year of measurement	2012	2015	2010-2012		2008-2014	2016-2018
Release factor wastewater						
Maximum	7.30%	2.21%	2.10%	2.1-7.3%	4.5%	2.76% (based on LoQ)
Geometric mean (GM)		2.21%	0.388%	0.39-2.4%	0.039%	1.38% (based on ½ LoQ)
Arithmetic mean (AM)	2.43%	2.21 (%)			0.14%	

* Site operating reduction of Cr(VI) prior to discharge; value given in original survey data.

** This site operated another unit with chromium releases unrelated to the use applied for until early 2014; measurements for previous years were therefore somewhat higher. This other unit has been dismantled and is no longer in operation. Release factors were therefore based on weekly measurements for the first six months of 2015. All measurements were below the LoD (20 µg/L for Cr(VI) and 50 µg/L (total Cr)) in 2015 and Cr(VI) concentrations were set to one half the LoD (10 µg/L) for the calculation of the release factor.

Both the mean values and the maximum values for sites A-E show a good level of agreement. It must be noted that all sites are in different countries and belong to different companies, producing quite different amounts of sodium chlorate (details not given here due to confidentiality). The values for site E are driven by the rather high LoQ for Cr(VI) of 50 µg/L. Nonetheless they fit very well into the range of the other sites. The average (AM and GM) values can be compared with release factors approximated from the information provided in the IPPC reference document (EC, 2007):

<u>Normalised to 1 t sodium chlorate</u>	<u>Minimum</u>	<u>Maximum</u>	
Amount SD used	10 g	150 g	IPPC reference document (EC, 2007)
Amount SD released to wastewater	0.1 g	3 g	IPPC reference document (EC, 2007)
Release factor wastewater	1%	2%	Calculated from values above

The site-specific average values (AM or GM: 0.39-2.4%) agree well with the release factors of 1-2% derived from the IPPC reference document. Again, the difference observed in the release factors calculated for the three sites does not necessarily relate to differences in process design, since natural chromium concentrations may (via process waters used at a site) impact the concentration in the STP effluent. The release factor for site B is based on one half the LoD and true releases may therefore be substantially lower. Likely, the release factor for site E is based on ½ of the LoQ and true releases are most probably substantially lower due to the reduction system applied. As a worst case the maximum release factor is given based on the full LoQ (50 µg/L).

We therefore conclude that the figures derived for the applicant's site E (CB, representative for SCB) are very well represented by sites A to C assessed in the earlier AfA. These figures are thus judged to represent a range that covers the use of SD by all companies of the sodium dichromate consortium irrespective of the presence or absence (Site B and Site E, i.e. SCB) of a biological STP. Also note that the 3 sites used for this assessment cover 2 sites using the highest amounts of SD per year (of all sites producing sodium chlorate). The average release factor for each site (AM or GM) was used since (a) release factors are based on a substantial dataset, (b) a chronic exposure estimate is required and (c) the average values are in agreement with the ones reported in the IPPC reference document (EC, 2007).

Exposure of humans via the environment will therefore be estimated for these 3 sites and in addition for the applicant's site E using site-specific tonnage information, release factors and site-specific information on STP discharge rates and river flow rates (see Annex 3C for details). While individual data for the other sites are not necessarily confidential, they are not disclosed here in order to prevent back calculation of amounts of SD used per site.

While EUSES requires some adaptation of the release factors used as input data⁴, note that the assessment is based on monitoring data obtained in the effluent prior to discharge into the water compartment. Since such measurements are independent of assumptions on the behaviour of a substance in the STP (in contrast e.g. to measurements in process streams before the STP), the ultimate release estimated is considered very reliable.

For one of the sites A to C and the applicant's site E, these site-specific data result in a dilution factor > 1 000 (< 1 000 for the other two sites; for site E slightly above 1 000 based on the mean waste water flow; 900 based on the maximum capacity of the chemical waste water treatment system). Dilution factors of more than 1 000 in surface waters should not be used according to the ECHA Guidance on environmental exposure estimation (ECHA, 2016), since the mixing zone may be very large in these cases. However, the site-specific dilution factors were used in the present case since (a) no environmental assessment (i.e. toxicity to fish, for example) is performed, (b) drinking water abstraction is the predominant pathway (see below), for which complete mixing can be assumed to have taken place.

Releases to soil

No substance is released to soil from the use covered by this CSR. As outlined in section 9.0.1 and in EC (2007) the process is carried out in a closed loop from an environmental point of view. I.e. samples and brine drainage are returned to the brine circuit, about [REDACTED] of process water is recycled to the process, cleaning water is recovered by a drainage system installed and treated. Additionally, areas where SD-containing brine is handled are equipped with fluid-barriers, which prevent uncontrolled leakage of SD containing brine and ascertain the recirculation to the process (see box above "Technical innovations introduced into the new SCB site").

Other input values

The input values for physico-chemical and environmental fate properties of SD were all taken from the EU Risk Assessment Report (ECB, 2005).

Table 3. Input data for sodium dichromate in EUSES modelling

Parameter	Value	Comment
Molecular weight	262 g/mol	
Melting point	357 °C	Refers to salt; SD becomes anhydrous at 100°C (ECB, 2005)
Boiling point	500 °C	SD decomposes above 400 °C (ECB, 2005)
Vapour pressure	0.00001 Pa	N/A; dummy value entered
Log Kow	0	N/A; dummy value entered
Water solubility	2 355 g/L	
Bioconcentration factor fish	1 L/kg	Value used in ECB (2005)
Kp <i>suspended matter</i>	1 100 L/kg	Mean of values in ECB (2005); see text for details
Kp <i>sediment</i>	550 L/kg	Mean of values in ECB (2005); see text for details
Kp <i>soil</i>	26 L/kg	Mean of values in ECB (2005); see text for details

The partition coefficients used for suspended matter, sediment and soil are the means of the two values used in ECB (2005) for Cr(VI) for these compartments. These are:

	<u>Acid conditions (pH ≤ 5)</u>	<u>Alkaline conditions (pH ≥ 6)</u>
Kp <i>suspended matter</i>	2 000 L/kg	200 L/kg

⁴ The release factors shown in Table 2 refer to the release in the effluent before entering the water compartment (i.e. after the STP). EUSES requires release factors from the process, i.e. before the STP. Since 50% removal of the substance is assumed following the approach in the EU RAR (see below), the release factor from the process is 2-times higher than the value given in the table. This is entirely a technical issue for EUSES modelling. In all cases, the modelled concentration in the effluent (after the STP) is identical to the monitored values that were used as the basis in deriving release factors.

Kp <i>sediment</i>	1 000 L/kg	100 L/kg
Kp <i>soil</i>	50 L/kg	2 L/kg

The mean of the value under acidic and alkaline conditions was used in the present assessment, since (a) it reflects the range of values and (b) the underlying data – especially for Kp *suspended matter* and Kp *sediment* – are not very well founded, preventing a more reliable estimate of these parameters.

Finally, removal during biological wastewater treatment (where applicable – i.e. not for sites B and E = SCB) was adapted according to the EU Risk Assessment Report (ECB, 2005) that assumed 50% release in the effluent and 50% adsorbed onto sewage sludge for Cr(VI). No application of sludge to soil from this industrial use was assumed based on survey data.

Regional and local assessments

Human exposure via the environment from consumption of drinking water, fish and via air (for rationale see above) is modelled both for the regional and the local scale. Many of the sodium chlorate producing sites are in different countries and even if within one country, they are several hundred kilometres apart. However, there are three cases where two sites are within a 100-200 kilometre radius and are thus within the same region as the site assessed (the region defined by EUSES covers 40 000 km²). As a consequence, the assessment performed for sites A-C covers a second site within the same region. The maximum SD tonnage of all sites other than sites A-C was used for this second site within a region. This does not represent reality and represents a worst case approach. For this applicant's site (site E) it is known that no other sodium chlorate producing sites do exist within the region. Therefore, no second site is covered in the corresponding regional assessment using EUSES.

9.0.2.3. Workers

Scope and type of assessment

The scope of exposure assessment and type of risk characterisation required for workers are described in the following table based on the hazard conclusions presented in section 5.11.

Table 4. Type of risk characterisation required for workers

Route	Type of effect	Type of risk characterisation	Hazard conclusion (see section 5.11)
Inhalation	Systemic, long-term	Not needed	DNEL (Derived No Effect Level) = 43 µg Cr(VI)/m ³
	Systemic, acute	Qualitative	High hazard (no threshold derived)
	Local, long-term	Semi-quantitative	DMEL (Derived Minimum Effect Level) = 0.0025 µg/m ³
	Local, acute	Qualitative	Moderate hazard (no threshold derived)
Dermal	Systemic, long-term	Quantitative	DNEL (Derived No Effect Level) = 43 µg/kg bw/d
	Systemic, acute	Not needed	No hazard identified
	Local, long-term	Qualitative	Moderate hazard (no threshold derived))
	Local, acute	Qualitative	Moderate hazard (no threshold derived))
Eye	Local	Qualitative	Moderate hazard (no threshold derived)

Comments on assessment approach:

General approach

Use of SD as an additive for suppressing parasitic reactions and oxygen evolution, pH buffering and cathode corrosion protection in the electrolytic manufacture of sodium chlorite. No professional or consumer uses are applied for in this application for authorisation and are therefore not part of this chemical safety report.

A potential for exposure may exist during the specific tasks identified below, basically reflecting sampling and loading tasks as well as maintenance tasks, and cleaning. Potential exposure during the handling of waste will be reduced by the use of a ceramic candle filter instead of a filter press (see also box above “Technical innovations introduced into the new SCB site”). Based on the process characteristics and properties of SD as a non-volatile substance, all potential inhalation exposure will be towards an aerosol/dust containing SD and all potential dermal exposure will be towards the SD dissolved in liquids.

As outlined below carcinogenicity is the most critical endpoint for risk assessment. According to the Risk Assessment Committee (RAC) “there are no data to indicate that dermal exposure to Cr(VI) compounds presents a cancer risk to humans” (ECHA, 2013). Therefore, the main focus of the quantitative exposure estimation and risk characterisation for inhalation exposure of workers is on carcinogenic effects. A quantitative dermal exposure assessment and risk characterisation with respect to effects on reproduction is performed in section 9.2.

A qualitative risk characterisation with respect to the corrosive and skin sensitising properties of SD is not part of this CSR, as SD has been included into Annex XIV to Regulation (EC) No 1907/2006 (REACH) due to its carcinogenic and mutagenic properties. According to REACH, Article 62(4)(d), the CSR supporting an AfA needs to cover only those potential risks arising from the intrinsic properties specified in Annex XIV. The applicant duly applies risk management measures derived by the registrant of SD due to other substance properties related to human health concerns and communicated via the SDS.

In general, reliable and representative measured data are favoured in an assessment of occupational exposure to chemicals. For a carcinogen such as SD, this is all the more desirable and some effort was undertaken to obtain such data. However, the following issues must be taken into account:

- Chromium exposure was previously monitored in the companies of the former consortium which produce sodium chlorate to show compliance with national legislation, but either
 - biological monitoring was performed that does not allow a differentiation between Cr(III) and Cr(VI) (Drexler and Hartwig, 2009) and is therefore unsuitable for the assessment in this report (i.e. a comparison with the exposure-risk relationship (ERR)). In addition, total chromium levels in biomonitoring studies are also highly influenced by several other factors than occupational exposure (geographical region, smoking status, intake from food and drinking water etc.) making an interpretation of obtained values from several different countries difficult to impossible in the absence of data on the background exposure.
 - air monitoring was performed with a limit of quantification (LoQ) adequate to demonstrate compliance with national occupational exposure limit values (OELs) that generally range between 10 000-50 000 ng/m³, with more recent values at 1 000 ng/m³ (see Annex 1). As a consequence, several monitoring results in the companies of the sodium chlorate consortium exist that identify Cr(VI) concentrations below a certain threshold, e.g. <2 000 or <5 000 ng/m³. With the 10⁻⁵ risk being associated with an exposure to 2.5 ng/m³ according to ECHA (2013), these air monitoring results were considered inappropriate in the context of this assessment. In addition, adequate documentation for these older measurements is often difficult to obtain.
- Personal monitoring was considered to be the best sampling method for inhalation exposure assessment. An overview of air monitoring methods for Cr(VI)⁵ indicated LoQs that are clearly above the concentration associated with a 10⁻⁵ risk (2.5 ng/m³ according to ECHA (2013)). During the former AfA a laboratory accredited for performing occupational monitoring (Eurofins GfA, Münster, Germany) was contacted and asked for the lowest LoQ achievable by personal sampling. The lowest LoQ was given as 250 ng/m³ (assuming little influence by matrix effects from the actual workplaces), a value that is in agreement with those given in the overview mentioned above. The dilemma that the LoQ of current monitoring methods is two orders of magnitude higher than the values derived from exposure-risk relationships has also been recognised by others. For example, Hahn et al. (2013) noted the current monitoring methods for carcinogenic metals (including Cr(VI)) are unable to measure the low concentrations (ng/m³ range) derived from exposure-risk relationships.

Company specific monitoring data for SCB Bussi could not be generated before the authorisation is granted. But company specific monitoring data for the Caffaro Brescia site are available (see Annex 3B). To reach a low limit of detection extended air sampling was performed (e.g. 3 h, 5 h) using high volume pumps. This enabled the CB to reach limits of detection in the range of 0.02 to 0.1 µg/m³. Single measurements for one task (filter press) were performed using long term (29 h) high volume sampling which resulted in a LoD of 0.3 or 0.4 ng/m³. All the measurements performed showed that the exposure was below the LoD, but the LoD except for

⁵ See e.g. <http://amcaw.ifa.dguv.de/substance%5Cmethoden%5C116-L-Chromium%20VI.pdf>

measurements near the filter press was at least one order of magnitude higher than the concentration associated with a 10^{-5} risk (2.5 ng/m^3 according to ECHA (2013)). Also the biomonitoring data were not sufficiently sensitive to verify an exposure at a concentration associated with a 10^{-5} risk.

On the basis of these considerations, a European-wide air monitoring campaign with static sampling was initiated by the chlorate producing companies during the former AfA. The monitoring campaign served two purposes:

- Obtaining reliable information on Cr(VI) concentrations in workplace air to be used in the risk characterisation for the use of SD covered by this CSR
- Identifying tasks and processes associated with high Cr(VI) concentrations that require changes in the procedures and/or additional risk management measures.

Since static monitoring may not be entirely representative of the exposure of workers (i.e. breathing zone concentrations), inhalation exposure was also modelled using a higher tier tool.

Air monitoring approach

As outlined above, air monitoring during the former AfA was performed using stationary sampling to achieve a sufficiently low limit of quantification. All sampling was performed to reflect exposure during the tasks described below. Basically, the monitoring campaign was conducted in the following way:

- Samples were collected between January and February 2015 at 8 sites in 5 European countries, all belonging to the chlorate producing companies. Although the companies applying for authorisation run a total of 12 sites only 8 sites were selected for monitoring as processes are comparable at different sites of companies running several sites. Monitoring at two sites of two companies with several sites revealed that this assumption was true. Note, however, that all companies were covered.
- All sampling and analyses were performed by Eurofins GfA (Münster, Germany), a company fully accredited in Germany to performing workplace measurements. Apart from Eurofins staff performing the sampling, consultants performing the higher tier modelling and the overall exposure and risk assessment were also present during the monitoring in order to a) obtain additional input parameters for the modelling and b) place the monitoring pumps with respect to the relevant tasks, thus ensuring that monitored and modelled exposure estimates refer to the same situation.
- The monitoring pumps were located as close to a potential source of worker exposure (e.g. a sampling outlet) or the worker as possible. This design deviates from “classic” stationary sampling, which often aims to measure concentrations in general work areas (e.g. with an impact of several sources), rather than task-specific concentrations (which would typically be measured by personal monitoring). While the position of the monitoring pumps was often within 1 m of the position of the worker when performing the task (e.g. sampling), such a close position could not be achieved in all cases. Safety considerations limited the possible positions, e.g. since emergency exits had to be kept clear and extension cables (required for the power supply of the monitoring pumps) were limited to certain areas to ensure the safety of the workplaces. In addition, the sampling devices had to be positioned in a way that did not prevent workers from carrying out the activities in their usual work routine, since this could lead to unrepresentative monitoring results. On the other hand, the source of exposure was sometimes contained towards the worker, while having an uncontained connection to the surrounding air away from the worker. The monitoring pump was then located at this latter point. These settings may in some cases underestimate or overestimate the concentration in the breathing zone of the worker.
- At each of these stationary monitoring points, sampling was performed over 8 hours, which resulted in a sampled volume of ($22.5 \text{ m}^3/\text{hour} \times 8 \text{ h} =$) 180 m^3 . The limit of quantification for Cr(VI) in air was 2.4 ng/m^3 . Dust sampling on crystal filters was performed with high volume samplers (Gravikon VC25). Chromium (VI) was analysed by UV/VIS spectrometry after elution and complexation with diphenyl carbazide. This methodology is based on the German standard methodology for Cr(VI) workplace measurement (IFA 6665) which was modified in the way that the sampling volume was increased to decrease the LoQ. Dust collection on crystal filters has the advantage that the samples can easily be transported to the laboratory. Therefore and due to the shorter sampling period (8 h vs 24 h), this approach is regarded superior to the methodology reported by Gladtko (2012) who used sample collection in fluids by using impingers. Stability of Cr(VI) on the filters during transport and analysis had been proofed by analysis of control filters, spiked with Cr(VI) (see Annex 2 for full details of the sampling and analytical methods).
- While sampling over such an extended period of time was necessary in order to achieve a limit of quantification in the range of exposure concentrations associated with low risks in the range of 10^{-5} , none of

the workers is close to these monitoring points for the entire shift or even for most part of the shift. In fact, for daily tasks such as sampling (task 2 below), workers often only spend about 1 minute directly at the sampling outlet and move on to the next sampling outlet or return to the production lab where the sample is analysed. Overall, workers spend most of the time in the control room, without performing specific tasks potentially associated with SD exposure.

- Due to the specific use of SD (handled at very low concentrations in aqueous solutions, no occurrence of SD powder) low Cr(VI) concentrations were expected. This expectation not only led to the choice of static monitoring (to achieve a sufficiently low LoQ), but also required to monitor the background concentration of Cr(VI), since levels of up to about 8 ng Cr(VI)/m³ may be found as a background concentration in industrial areas, e.g. due to emissions from stainless steel factories (Gladtko et al., 2012; Scott et al., 1997). Therefore, ambient samples were taken at seven sites (impossible to perform at one site). The monitoring pumps for the ambient samples were positioned about 50-100 m upwind of the chlorate unit to cover emissions from other sources. Wind direction was not measured as part of the monitoring campaign, but was judged visually from wind vanes or anemometer recordings present at sites.
- The data generated by the monitoring campaign relate to the conditions present at the time of monitoring (January-February 2015). One of the aims of this monitoring campaign was to identify processes associated with the highest exposure. In fact, consultants already discussed the exposure potential of specific processes with company representatives during the monitoring campaign. On the basis of the monitoring results, some processes associated with elevated Cr(VI) concentrations came under review and were changed. Other processes are still under review for possible changes of process design or additional risk management measures.
- At each plant, sampling was performed on two consecutive days with 5 samples taken each day (typically from 10:30-18:30 on the first day and from 8:30-16:30 on the second day). Since shifts generally change during daytime and different shift workers are often involved on two consecutive days, this approach also reflects between-worker variability for tasks performed by each shift (i.e. sampling and production lab analyses; see below). Overall, the total number of samples was 10 per site, resulting in 80 samples overall. Of these, 14 samples were obtained from ambient monitoring points and 66 samples involved tasks with potential exposure to Cr(VI) during sodium chlorate production.
- All monitoring data from all sites are assessed together and the pooled data per task form the basis of the exposure assessment (where sufficient). While the data for individual companies are reported in Annex 3B, no site-specific assessment of occupational exposure was performed. Such an approach has the advantage of providing a higher number of samples for routine tasks, while at the same time covering variation in exposure patterns.

As stated above, workers only spend a limited time at the points where monitoring was performed (i.e. at sampling outlets, in the production lab etc.). Unit operators typically spend most of the shift in the control room (Figures A4-1 and A4-2 in Annex 4), visually controlling and adjusting the operation of the processes. In addition, processes and equipment in the unit are checked from time to time. Such control visits in the unit are limited in terms of the time spent since the chlorate unit represents a noisy and sometimes warm environment. As a consequence, the monitoring result for a specific task is converted to a TWA under consideration of the exposure duration for that task:

$$\text{TWA} = \text{monitoring result} \times \text{exposure duration [min/shift]} / 480 \text{ min}$$

The issue of averaging exposures over the shift is discussed in more detail in section 9.1.6.1.

For tasks not performed on a daily basis (tasks 1 and 4; see below), the long-term TWA is calculated under consideration of the task frequency:

$$\text{Long-term TWA} = \text{TWA [ng/m}^3\text{]} \times \text{frequency [d/a]} / 240 \text{ d/a}$$

Note that such a “dilution” over the entire year for infrequent tasks is feasible for the endpoint of carcinogenicity, but may not be adequate for other endpoints. The exposure estimate is therefore confined to this endpoint.

Modelling approach for inhalation exposure

Occupational exposure for the inhalation pathway was modelled with ART (Advanced REACH Tool, version 1.5, <http://www.advancedreachtool.com>) that is considered a higher tier tool in the ECHA Guidance IR & CSA,

Ch. R.14 (ECHA, 2012b). It allows more adequately reflecting real conditions of use than lower tier tools such as ECETOC TRA. In addition, SD is dissolved in a liquid during all activities related to this use, a situation that is outside the applicability domain of ECETOC TRA (ECETOC, 2012). For all tasks, the following principal approach was chosen:

- Exposure was modelled as “near field exposure” within ART, i.e. the worker is assumed to be less than 1 m from the emission source for the entire exposure duration assumed.
- The upper inter-quartile confidence interval of the 75th percentile is used as the exposure estimate. This approach follows the recommendations of the developers of the tool. This value better accounts for uncertainty and variability in the underlying data than e.g. the 90th percentile. However, both measures often result in similar values.
- Exposure was modelled in ART as a task-based concentration (assuming exposure duration = 480 min) that was then converted outside the tool to time-weighted average (TWA) on the day of exposure considering the exposure duration for the specific task:
 - $TWA = \text{task-based concentration} \times \text{exposure duration [min/shift]}/480 \text{ min}$
 - This algorithm is identical to the one applied in ART, if the TWA is modelled rather than the task-based concentration).
- The long-term TWA was then calculated outside the tool, taking into account the frequency of each task:
 $\text{Long-term TWA} = TWA [\text{ng/m}^3] \times \text{frequency [d/a]} / 240 \text{ d/a}$
 As discussed above, such a “dilution” over the entire year is limited to the endpoint of carcinogenicity.

The estimated long-term TWA for the different tasks were combined in aggregated exposure estimates, since a single shift operator may perform more than one task during a shift. It is, however, unlikely that a single worker will perform all tasks with the assigned frequency in a given year. This issue is addressed in more detail in the aggregated exposure assessment in section 9.1.6.

Definition of tasks

The use of SD in sodium chlorite production is essentially in a closed-loop process with no exposure of workers being expected during the general processing steps for the following reasons (based on EC, 2007):

- Closed-loop process with a high degree of closure and recycling of SD
- SD emission from the process may occur through water and solid waste, but
 - SD in the aqueous phase shows no potential for dust exposure,
 - the solid waste consists of a slurry/filter cake with no potential for dust generation.

The entire process of SD use in sodium chlorate or chlorite production can best be described by PROC 3 according to ECHA Guidance (ECHA, 2010):

*“Use in closed batch process (synthesis or formulation): Batch manufacture of a chemical or formulation where the predominant handling is in a contained manner, e.g. through enclosed transfers, but where **some opportunity for contact with chemicals occurs, e.g. through sampling**” (our emphasis).*

Based on a general understanding of the processes involved, the answers in the questionnaires filled in by all sodium chlorate producing companies of the consortium and ten plant visits by the consultants performing the exposure assessments, the following specific tasks were identified as being potentially associated with exposure (**Table 5**). These tasks are described in more details below. Note: For the Caffaro Brescia site additional sampling and laboratory analysis of the sodium chlorite production unit were regarded as the SD concentration in the solutions of the sodium chlorite production were higher than in the sodium chlorate brine. Due to the technical improvements at the SCB Bussi site these additional tasks have not to be considered for this AfA, as the SD concentration does not show a relevant increase in the chlorine dioxide generator.

Table 5. Task definition

Task	Description
Task 1 (T1)	Feeding liquid SD solution into the process (PROC 8b)
Task 2 (T2)	Use in closed batch process: Sampling electrolyte solution (PROC 3)

Task 3 (T3)	Laboratory analyses (production lab) (PROC 15)
Task 4 (T4)	Maintenance and cleaning (PROC 8a)
Task 5 (T5)	Laboratory analyses (central lab) (PROC 15)

Sampling is considered to be covered by the PROC 3 definition from ECHA (2010) and was therefore assigned this PROC, rather than e.g. PROC 8a. However, the transfer of the concentrated SD solution as well as the waste handling operation were considered to be better characterised by PROC 8b. Note that this transfer of the concentrated SD solution is also within a closed system and exposure is only related to connection and disconnection of pumping or piping systems. Maintenance and cleaning activities were described by PROC 8a. Finally, PROC 15 was assigned to laboratory activities performed by unit operators in a production lab (task 3) and by laboratory staff at all sites (task 5).

The PROCs given in **Table 5** are only a surrogate and are irrelevant in the exposure assessment presented below, since this is based on air monitoring and modelling using the ART. Both air monitoring and ART modelling are entirely independent of PROCs (see above for details on the approach to exposure estimation).

The individual tasks are described in more detail in the following sections that also describe the general modelling input for ART (e.g. activity classes, containment levels assumed). Full ART reports are attached in Annex 5. More specific input parameters (e.g. Cr(VI) concentration, exposure duration and frequency) are described below in the section on “critical input parameters”.

Whenever gloves and respiratory protective equipment (RPE) are mentioned in the task description below, these refer to:

Gloves: A variety of material is suited for protection against SD in aqueous solutions (breakthrough time ≥ 8 h for all):

Natural rubber/Natural latex (0.5 mm)

Polychloroprene (0.5 mm)

Nitrile rubber/Nitrile latex (0.35 mm)

Butyl rubber (0.5 mm)

Fluoro carbon rubber (0.4 mm)

Polyvinyl chloride (0.5 mm)

RPE: Half mask or full mask with P3 filter or full mask with P3 combination filter, the assigned protection factors (APF) are 20 (half mask) and 40 (full mask) according to Howie (2005). If P3 combination filters are used, the APF is lower by a factor of 2, e.g. APF is 20 for full mask with P3 combination filters. Half masks with P3 combination filters are not supported since they do not provide the APF of 20 used in exposure estimation.

Additional PPEs like goggles or face shields are not addressed in detail here, as they have no impact on inhalation exposure modelling. But, of course they are used during the handling of (corrosive) liquids.

T1: Feeding liquid SD solution into the process

As a principal risk management measure, all sites (including the future SCB site) use liquid SD concentrate rather than solid SD, thus preventing any exposure to neat SD dust. Feeding the concentrate into the process from an IBC containing the SD concentrate is essentially an automatic and closed process. An exposure potential exists, when connecting and disconnecting pipes/hoses, but this is assumed to exist only from small amounts of liquid remaining on the transfer equipment (pipes, pumps depending on the process) while connecting/disconnecting the equipment. Within ART, this situation was modelled as a “handling of contaminated objects” with small surfaces ($<0.1 \text{ m}^2$) being contaminated to a small degree ($<10\%$). These parameters were selected to reflect a surface area of up to $30 \text{ cm} \times 30 \text{ cm}$ (0.09 m^2) for connecting ends of pipes/hoses (these are much smaller, and the lowest value of ART was chosen). A low level of contamination was chosen, since special care is taken when handling the concentrated SD solution that not only possesses carcinogenic properties, but is also corrosive.

PPE: Gloves and respiratory protection are worn during this task and a protective apron is recommended in case contact with the IBC is likely.

Task 1 is an infrequent task performed up to about twice a month at some sites, but less often at other sites (including the future SCB site) (see section “Critical input parameters” below). It is also worth noting, that some sites operate dosing pumps that are fixed to the IBC containing the SD concentrate. In these cases, connecting/disconnecting the equipment occurs only when the IBC is empty and a new IBC is connected (about 1/year or less often). At other sites, the IBC is connected to the process each time that feeding of SD into the process is required (compare Figures A4-3 and A4-4 in Annex 4).

T2: Use in closed batch process: Sampling and, T3: Laboratory analyses (production lab)

These tasks concern the electrolyte solution and T2 and T3 are performed daily, generally by the same staff members (unit operators). Within ART, both tasks were modelled as a “transfer of liquid products – falling liquids”. For the future SCB site it is envisaged that the unit operators will take all the samples. Laboratory analysis will be performed during the normal workday by the central laboratory workers. During the early morning and the night shifts and weekends the unit operators will perform the laboratory analysis.

For both tasks, “handling that reduces contact between product and adjacent air” and “submerged loading” were selected in ART, since relatively small amounts of liquid are carefully transferred into bottles with a small opening. The visits of all sites included in the monitoring campaign demonstrated that sampling is sometimes performed under less stringent conditions. This is largely due to the fact that the electrolyte solution easily crystallises due to its high salt content. For this reason, flushing of the sampling outlet is required before taking the samples (this also results in more representative samples) and a more open process design is in operation at some plants. However, in the light of the extremely conservative assumptions already applied in the modelling (i.e. assumption of maximum SD concentration, application of the entire task duration to the “falling liquid” duration, upper end of the ART transfer rate two-times above the maximum of real transfer rates), the stricter conditions are retained in ART modelling.

No localised controls were assumed in ART modelling for sodium chlorate production lab analyses (task 3) in the former CB AfA. In the former AfA production lab analyses were performed at some sites outside the fume cupboard (see e.g. Figure A4-13 in Annex 4), no localised controls were assumed in the general approach. The assumption of no localised controls for all analyses nonetheless added another conservative element to the estimate to the ART estimates. However, efficient exposure reduction due to the future use of a fume cupboard was considered for SCB. Overall, consideration of this task is a conservative approach, as sampling in the context of laboratory work is outside the scope of AfA.

PPE: Gloves are worn during this task.

T4: Maintenance and cleaning

Some maintenance tasks with potential exposure to SD (e.g. cleaning reaction vessels, cell rooms etc.) are very rare (less than once per month), while others may occur at a higher frequency (e.g. change of pumps, valves etc.). Therefore, these latter activities are addressed in the exposure assessment under the assumption of a relatively high frequency (see section “Critical input parameters” below). Within ART, this situation was modelled as a “handling of contaminated objects” with small-medium surfaces (0.1-0.3 m²) that are contaminated to a considerable degree (10-90%). The surface area was chosen to cover areas of up to about 55 cm x 55 cm (0.303 m²), believed to represent connecting ends of larger pumps. The degree of contamination was selected to represent substantial contamination of this area.

Other activities, e.g. cleaning of equipment with a water hose, as observed during the monitoring campaign, cannot be adequately modelled with ART. However, these activities were monitored during the monitoring campaign. Duration and frequency for tasks such as cleaning with a water hose (considered to be critical due to aerosol generation) differ between companies. A total duration of 120 minutes per workweek (e.g. for about 20 min every day or for 60 min twice a week represent a worst case across companies).

Note that the survey data for duration and frequency regularly related to overall values and not to those relevant for SD exposure. For companies, it was very difficult to assign specific values, since many of these tasks relate to activities that are performed on an ad-hoc basis. A differentiation between overall task duration and the specific activities related to Cr(VI) exposure was impossible. In the light of these issues, more realistic estimates for the task duration and frequency were derived below.

PPE: Respiratory protection (half mask or full mask with P3 filter or full mask with P3 combination filter) in the case of aerosol formation (e.g. cleaning with a water hose); gloves are worn during this task as well as tight, long apron and boots or suitable chemical protection suit in the case of aerosol generation.

Waste handling (filter press) – T5 in the former CB AfA, not relevant for the SCB Bussi site

Solidified material has to be removed from the process from time to time and sent to special waste treatment. This involves processing of the slurry through a filter press that automatically separates solid and liquid fractions, the latter being recycled into the system. Filter presses are marketed as fully automatic systems and are supposed to run without intervention by the workers. Generally, the filter cake is removed from the press by gravity without any intervention by workers. In practice, however, workers have to scrape off some of the filter cake with a tool from time to time. The cake is still very wet (otherwise gravity would not work) and exposure modelling within ART was therefore performed as “Paste, slurry or clearly (soaked) wet powder – Handling of contaminated solid objects or paste” that are not contaminated with powdered material in the former CB CSR.

This worker contributing scenario assessed in the former CB AfA is not relevant for the SCB Bussi site as the filter press will be removed by a ceramic candle filter (see also box above “Technical innovations introduced into the new SCB site”). The ceramic candle filter will require only very seldom maintenance activities. Before the maintenance activities take place the brine will be removed from the candle filter and the ceramic filter will be washed. It is currently assumed that the washes will result in a 10fold dilution of the Cr(VI) in any remaining brine. Due to this low concentration (probably <0.02%, i.e. outside the scope of AfA) and the very seldom frequency this activity is not considered as a task which contributes in a relevant manner to workers exposure.

T5: Laboratory analyses (central lab)

Analyses in a central lab are performed by other personnel than unit operators (i.e. lab technicians) and exposure is therefore modelled separately, assuming operation of a typical laboratory fume cupboard. Similar to T3, this task was modelled as a “transfer of liquid products – falling liquids” (see section “Critical input parameters” below). The containment was set to “handling that reduces contact between product and adjacent air” as the liquid is typically transferred in small amounts with pipettes or similar equipment. The loading type was set to “splash loading” to obtain a more conservative estimate. Overall, consideration of this task is a conservative approach, as laboratory work is outside the scope of AfA.

PPE: Gloves are worn during this task.

Critical input parameters

The critical input parameter values described in this section are largely based on a survey conducted by the consultants performing the exposure assessment for a consortium of chlorate producing companies (data obtained in several rounds 2013-2014, with additional e-mail surveys on specific parameter inputs). In addition, ten site visits by the same consultants were performed to gain a better understanding of the processes, conditions and risk management measures in place. In preparation of this AfA also the CB site was visited and the critical parameters for the future plant were collected by a questionnaire. Data generated from the former surveys and site visits were collectively referenced as “survey” in the following tables. Note that median and maximum values are reported in the tables whenever available, but that the overall number of data points was considered insufficient to derive upper percentile values and to run a probabilistic assessment. Rather, the following approach was selected for the input values (except where indicated otherwise):

- maximum values for the SD concentration (and Cr(VI) concentration calculated from it)
- maximum value for the exposure duration (conservative TWA on the day of exposure)
- maximum value for the task frequency (conservative long-term TWA estimate)
- median values for most of the other input parameters (e.g. room volume); 10 air changes per hour (ACH) were assumed as a typical value for industrial settings (apart from T3 and T5: 3 ACH). A ‘median’ value of 10 ACH was selected, since operation is carried out in open spaces at some sites (e.g. in halls with one of two sides completely open, resembling more roofed outside areas than closed halls) or with large doors of the hall being open for considerable periods. While this was not observed at all sites and clearly is dependent on weather conditions at some sites, this value was chosen in the light of the worst case (maximum) assumptions indicated above. In addition, the air changes per hour only have a limited effect on the near-field task-based concentration in large workrooms. For a room volume of 1000 m³, for example, the concentration modelled in ART with 0.3 ACH is only 1.4-times higher than the one modelled with 10 ACH for dusts/mists (i.e. low volatile liquids as is relevant here) during a 8-hour task (Fransman et al., 2010). Overall, we consider the use of these ‘median’ values appropriate when used together with maximum assumptions on the other parameters mentioned above. Laboratory work, especially at production site laboratories is often performed in small rooms with lower air exchanges. Therefore, a lower value of 3

ACH was selected for the calculation as it seems more appropriate than the value of 10 ACH.

SCB-specific parameters are also reported for an improved adaptation of the former exposure assessment on the future situation.

Table 6. Critical input parameters (bold print indicates values used in modelling)

	Unit	Range	Median	Max.	Best estimate for SCB/Bussi	Source/comment
Task 1						
SD concentration	%	60-70	61	70	67	Survey
Cr(VI) concentration	%	24-28	24	28	27	Calculated from SD concentration
Duration	min	2-120	30	120	30	Survey; values reflect pumping duration, maximum exposure during connection/ disconnection estimated to be 30 minutes (i.e. median value for pumping)
Frequency	d/a	0.5-24	6	24	6	Survey; the maximum value is no longer practiced since the process was changed; retained here since the second highest value is similar (20 d/a)
Room volume	m ³	>500-130000	1000	130000	Not applicable	Survey (SCB: The cells will be installed under a roof, but not in a completely closed room. Only in one side of the plant will be a wall. The whole floor of the plant is about 41 x 30 m for a height of about 12 m under the roof (14760 m ³ - see rendering). The first floor has steel grating flooring)
Task 2						
SD concentration	g/L	3-7		6.5	≤ 5	Survey; median not calculated because data were sometimes reported as ranges (since Cr(III) and Cr(VI) concentrations are variable in different process steps); 3-7 g/L given by one company in initial survey; 6.5 g/L SD considered maximum after clarification (██████).
Density of solution	g/L			1400	1260 - 1370	Minimum density from e-mail survey
SD concentration	%			0.464	0.36	Calculated from the above
Cr(VI) concentration	%			0.184	0.14	Calculated from the above
Duration	min	12-30	20	30	20	Survey; values were sometimes given per shift, sometimes per day, i.e. overestimate of shift-based value; values generally refer to overall duration and not to the duration of liquid flowing
Frequency	d/a			240	240	Daily
Room volume	m ³	100-130000	2500	130000	Not Applicable	1000 m³ assumed in ART, since the next possible option in ART (3000 m ³) is higher than the median
Transfer rate	L/min	0.02-0.5	0.15	0.5	0.5	Survey; calculated from sampling volume and duration reported in survey; 0.02 L/min considered too low; ART input 0.1-1 L/min (for “filling of bottles”) selected, covers maximum of survey data.
Task 3						

	Unit	Range	Median	Max.	Best estimate for SCB/Bussi	Source/comment
SD concentration	g/L			6.5	≤ 5	See task 2
Density of solution	g/L			1400	1260-1370	See task 2
Cr(VI) concentration	%			0.0922	0.07	Calculated from the above; 50% of calculated SD concentration (0.184%, see task 2) assumed due to rapid dilution in production lab; observations during site visits indicate that only two-fold dilution is worst case)
Duration	min	6-240	30	240	60	Survey; values were sometimes given per shift, sometimes per day, i.e. overestimate of shift-based value; no clear differentiation between production lab and central lab possible, but 30 minutes (median from all data) appears to be close to maximum for production lab analysis (240 minutes chosen for central lab, see task 5 below)
Frequency	d/a			240	240	Daily (SCB: On working days (240 days/year) the analysis of the samples taken during the work day will be performed by central lab)
Room volume	m ³	40-300	183	300	120	Any size workroom assumed in ART
Transfer rate	L/min	0.02-0.5	0.02	0.5	0.5	Survey; no clear differentiation between production lab and central lab possible; ART input of 0.1-1 L/min (for “filling of bottles”) covers maximum of survey data.
Task 4						
SD concentration	g/L			6.5	≤ 5	See task 2
Density of solution	g/L			1400	1260 - 1370	See task 2
Cr(VI) concentration	%			0.184	0.14	See task 2; pumps assumed to be contaminated with electrolyte solution.
Duration	min	60-720	480	720	60	Survey; values sometimes related to very rare tasks, sometimes to more frequent tasks without exposure potential; task duration is often substantially longer than exposure duration, i.e. the repair of pumps takes much longer than exposure to SD exist, since pumps are repaired after cleaning them from electrolyte solution; in addition, SD concentration during cleaning activities will rapidly decline due to dilution with water; 60 minutes with SD exposure during maintenance assumed considering that the SD concentration in the undiluted electrolyte is assumed. A duration/frequency of 120 min/week for cleaning with a water hose is considered to represent a worst case from survey data.

	Unit	Range	Median	Max.	Best estimate for SCB/Bussi	Source/comment
Frequency	d/a	6-240	18	240	48 (maintenance) 96 (cleaning)	Survey; values sometimes related to very rare tasks, sometimes to more frequent tasks without exposure potential; the value of 240 d/a refers to companies that indicated daily maintenance of any kind (typical maintenance tasks also relate e.g. to work on electrical components that does not involve exposure to SD); task frequency for tasks with potential Cr(VI) exposure assumed to be once a week (48/a); see “duration” above for cleaning activities.
Room volume	m ³	500-10000	1000	10000	Not Applicable	Survey
Task 5						
SD concentration	g/L			6.5	≤ 5	See task 2
Density of solution	g/L			1400	1260 - 1370	See task 2
Cr(VI) concentration	%			0.184	0.14	See task 2
Duration	min	6-240	30	240	240	See task 3 (SCB: conservative estimate, probably only ca. 80 min per day)
Frequency	d/a			240	240	Daily use assumed, although not daily at some sites
Room volume	m ³	40-800	300	800	150	Any size workroom assumed in ART
Transfer rate	L/min	0.02-0.5	0.02	0.5	0.5	See task 2; surveyed together with sampling; reported differences between sampling and lab analyses negligible and all values within ART input range of 0.1-1 L/min (for “filling of bottles”)

9.0.2.4. Consumers

Exposure assessment is not applicable as there are no consumer-related uses for the substance.

9.0.3. Exposure-risk relationships (ERRs) for carcinogenic effects and DNEL values for reproductive toxicity used for the assessment

Sodium dichromate has been included in Annex XIV of REACH due to its CMR properties as it is classified as carcinogenic (Cat. 1B), mutagenic (Cat. 1B) and reproductive toxicant (Cat. 1B). Sodium dichromate affects both, fertility and development. As outlined above (section 5.11) the inhalation DNEL values derived by RAC with respect to the effects on fertility are lower than the DNELs derived on basis of effects on developmental toxicity. Inhalation DNELs systemic long-term for fertility are several (5 or 6) orders of magnitude higher than the local inhalation DMELs associated with an excess risk of 1×10^{-5} or 1×10^{-6} as derived for workers or consumers, respectively. Excess cancer risk is therefore used for risk characterization for worker inhalation exposure. For comparison risk-characterisation ratios are also presented for the inhalation exposure. Worker dermal DNEL long-term systemic effects are applied for the risk characterization of dermal exposure, as no DMEL values are available for dermal exposure, because SD is not carcinogenic after dermal exposure. As mutagenicity is a mode of action expected to contribute to carcinogenicity mutagenic risk can be considered to be included in the assessment of carcinogenic risk and low risks for mutagenicity are expected for exposures associated with low carcinogenic risks. Therefore, carcinogenicity is regarded as the most critical endpoint for risk assessment and in the following only the carcinogenic risk of sodium dichromate exposure will be considered.

As detailed in Section 5.11, the exposure-risk relationships presented by ECHA (2013) are used for calculating risks associated with the use of SD covered by this application. The inhalation risk characterisation for workers is solely based on inhalation exposure and the risk for lung cancer, as there is no information on the fraction of inhalable, but non-respirable particles, preventing the differentiated consideration of inhalation and oral exposure of workers. This is also the default procedure proposed by ECHA (2013). The following exposure-risk relationships are used.

Table 7. Exposure-risk relationships for inhalation exposure of workers used for calculating risks due to SD exposure (from ECHA, 2013)

TWA Cr(VI) exposure concentration [$\mu\text{g}/\text{m}^3$]	Excess lung cancer risk in EU workers [$\times 10^{-3}$]
25	100
12.5	50
10	40
5	20
2.5	10
1	4
0.5	2
0.25	1
0.1	0.4
0.01	0.04

Table 8. Exposure-risk relationships for inhalation exposure of general population used for calculating risks due to SD exposure (from ECHA, 2013)

Ambient Cr(VI) exposure concentration [$\mu\text{g}/\text{m}^3$]	Excess lung cancer risk in the general population [$\times 10^{-3}$]
10	290
5	145
2.5	72
1	29
0.5	14
0.25	7
0.1	2.9
0.01	0.29
0.001	0.029
0.0001	0.0029

Table 9. Exposure-risk relationships for oral exposure of general population used for calculating risks due to SD exposure of humans via environment (from ECHA, 2013)

Constant average oral daily dose of Cr(VI) [$\mu\text{g}/\text{kg bw}/\text{day}$]	Excess small intestine cancer risk in the general population [$\times 10^{-4}$]
10	80
5	40
2.5	20
1	8
0.5	4
0.1	0.8

The risk characterisation for dermal exposure of workers is based on the DNEL derived by RAC (ECHA, 2015):

- dermal DNEL systemic long-term: $43 \mu\text{g CrVI}/\text{kg bw}/\text{d}$

The risk characterisation for oral and inhalation exposure of humans via the environment is based on the s derived by RAC (ECHA, 2015):

- inhalation DNEL systemic long-term: $11 \mu\text{g CrVI}/\text{m}^3$
- oral DNEL systemic long-term: $17 \mu\text{g CrVI}/\text{kg bw}/\text{d}$

9.1. Exposure scenario 1: Use at industrial site - Use of SD as an additive for suppressing parasitic reactions and oxygen evolution, pH buffering and cathode corrosion protection in the electrolytic manufacture of sodium chlorite

Production of sodium chlorite takes place in a closed loop, separated in two steps: sodium chlorate production and subsequent sodium chlorite production which are run at different locations of the plant. There is one additional sampling point in the sodium chlorite unit and an additional analysis of this sample which is additionally modelled (see below).

Sector of use:

SU 8, Manufacture of bulk, large scale chemicals (including petroleum products)

Environment contributing scenario(s):	
Not assessed	
Worker contributing scenario(s):	
T1: Feeding SD solution into the process	PROC 8b
T2: Use in closed batch process: Sampling of the electrolyte solution	PROC 3
T3: Production lab analyses	PROC 15
T4: Maintenance and cleaning	PROC 8a
T5: Central lab analyses	PROC 15

Overview of air monitoring results

The next sections present the detailed exposure assessment and risk characterisation for the specific tasks relevant for the use covered by this CSR. Before addressing the task-specific values, a general overview of the air monitoring results is presented in this section. **Table 10** shows a summary of the results of the air monitoring campaign. (The monitoring campaign also included the activities near the filter press, which will not be used at the planned SCB Bussi site.) A full statistical evaluation of the results of all sites is included in Annex 3A. These pooled data form the basis of the exposure assessment. Monitoring results collected by this applicant during workplace supervision are also provided in Annex 3B. The table also shows Cr(VI) concentrations based on an evaluation of the German MEGA database for comparison. The underlying data were measured by stationary sampling at German workplaces between 2000 and 2009⁶. These values were used here for comparison, since they were obtained with a uniform method, represent a large number of samples and sites monitored and clearly differentiate stationary sampling results from those obtained with personal sampling.

Table 10. Summary of air monitoring results

Type of sample	N (sites)	N	Cr(VI) measurements <LoQ	Air monitoring results:
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⁶ Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung (IFA): MEGA-Auswertungen zur Erstellung von Expositionsszenarien für Chrom(VI)-Verbindungen, http://www.dguv.de/medien/ifa/de/fac/reach/mega_auswertungen/chrom-VI-Verbindungen_d.pdf, accessed: March 2015

				Cr(VI) [ng/m ³]		
				AM	Median	90 P
All	8	80	65% (LoQ 2.4 ng/m ³)	18	1.2*	22
Ambient	7	14	100% (LoQ 2.4 ng/m ³)	1.2*	1.2*	N/A
All tasks	8	66	58% (LoQ 2.4 ng/m ³)	22	1.2*	24
All tasks, outliers removed**	8	62	61% (LoQ 2.4 ng/m ³)	8.6	1.2*	22
Values for comparison						
MEGA (DE, 2000-2009)***	806	1837	65% (LoQ 100 ng/m ³)	2933	<LoQ	3656

All values rounded to two significant figures for presentation, but unrounded values used for calculation of exposure.

AM: arithmetic mean; 90 P: 90th percentile; N (sites): Number of sites covered; N: Number of measurements

* Values below the limit of quantification (LoQ: 2.4 ng/m³) were taken here as one half the LoQ (1.2 ng/m³).

** See section 9.1.3 for details on removal of outlier values.

*** Values given as CrO₃ concentrations in the source were multiplied by a factor of 0.52 (based on molecular weights), resulting in the Cr(VI) concentrations given in the table.

The data in **Table 10** show that the monitoring results obtained during the monitoring campaign are very low. Mean and 90th percentile values are both two orders of magnitude lower than Cr(VI) concentrations measured at German workplaces between 2000 and 2009. This finding can be explained by the fact that the MEGA data cover several industries, including metal processing industries (which contribute about 75% of all stationary samples to the 1837 samples presented in **Table 10**). In contrast, the monitoring campaign performed in the context of the assessment presented here relates to a minor use of SD. As a consequence, the overall Cr(VI) concentrations measured are very low.

In fact, the AM of 8.6 ng/m³ for all tasks combined after exclusion of outliers (see section 9.1.3) is only slightly higher than the AM of 8.2 ng/m³ (n=33) reported from ambient monitoring 400 m downwind of a stainless steel factory in Krefeld, Germany (Gladtko et al., 2012). This further supports the notion that the Cr(VI) concentrations measured at workplaces during the use of SD assessed in this report are low, with mean values close to values occasionally observed in ambient monitoring due to industrial emissions alone.

The fraction of Cr(VI) measurements <LoQ during the monitoring campaign was slightly lower than in the MEGA dataset, when task-based values are considered (i.e. excluding the ambient monitoring). This finding is due to the much lower LoQ achieved during the monitoring campaign (2.4 ng/m³) when compared with the MEGA data (LoQ: 100 ng/m³).

The overall finding of low Cr(VI) concentrations reflects the fact that the sodium dichromate concentrations in the process are very low. In addition, sodium dichromate is exclusively used dissolved in aqueous solution, limiting the potential of the substance becoming airborne. In this context, it is also worth noting that the dust (inhalable fraction) concentrations observed during the monitoring campaign are low. For all task-related measurements (i.e. excluding the ambient samples), the mean dust concentration was 64.9 µg/m³ (median: 44.5 µg/m³; 90th percentile: 141 µg/m³; range: 0.719-439 µg/m³).

9.1.1. Environmental contributing scenario 1

As sodium dichromate is not listed in REACH Annex XIV due to environmental effects, no environmental exposure assessment is performed here. However, human exposure via the environment is assessed and the local releases assumed in this context are shown in the following table (see section 9.0.2.2 for a justification of these values).

Table 11. Local releases to the environment

Release	Release factor estimation method	Explanation / Justification
Water	Measured release (Site-specific data)	Final release factor: : 2.43% (Site

Release	Release factor estimation method	Explanation / Justification
		A), 2.21% (Site B) 0.388% (Site C), 1.379% (Site E)
Air	Estimated release (generic for sites covered by this CSR)	Final release factor: 0.000278% (Sites A-C), 0.000184% (Site E)
Soil	Release factor (Site-specific data)	Final release factor: 0%

The release factor for water is based on monitoring data specific for Cr(VI) from 3 sites covering 2 sites using the highest amounts of SD of all sites of the companies of the sodium chlorate consortium. In addition, the release factor for water for site E (SCB) is based on monitoring data specific for Cr(VI) from CB site, which is regarded as representative for SCB (site E) in a conservative way (reductive treatment of waste water; high background value for Cr(III and VI) for site CB). Release rates for sites A to C are not given here due to confidentiality reasons. Details on release and derivation of release factor for water for site E based on data from site CB can be found in Annex 3B. The release factor for air is based on worst case assumption for diffuse emissions from the process. The release factors are fully justified in section 9.0.2.2.

Exposure and risks for the environment and man via the environment

As sodium dichromate is not listed in REACH Annex XIV due to environmental effects, effects of the substance on the environment are not considered here.

Inhalation exposure of humans via the environment was assessed using a worst case approach based (a) on diffusive emissions calculated from data obtained during occupational monitoring close to sources (sampling points, cleaning activities etc., sites A-E) and (b) on dust emissions during drying of sodium chlorate crystals (sites A-C, only; at site E, sodium chlorate is not dried but further processed to sodium chlorite).

As shown in the following table, predicted environmental concentrations (PECs) of Cr(VI) in air at all sites are very low and even the local Cr(VI) PECs are one to two orders of magnitude lower than the limit of detection for Cr(VI) in ambient air samples of 0.45 ng/m³ as given by Gladtko et al. (2012). For site E, the local and regional PEC is about one order of magnitude lower compared to sites A-C. The reason is the lower exposure to air because of the immediate processing of sodium chlorate to sodium chlorite, i.e. no exposure due to drying of chlorate crystals at site E.

Table 12. Modelled exposure for humans via the environment: inhalation

	Site A	Site B	Site C	Site E
Regional Cr(VI) PEC in air [ng/m ³]	4.76 x 10 ⁻¹⁴	3.53 x 10 ⁻¹⁴	7.42 x 10 ⁻¹⁴	5.44 x 10 ⁻¹⁵
Local Cr(VI) PEC in air [ng/m ³]	2.86 x 10 ⁻⁰³	1.68 x 10 ⁻⁰³	5.88 x 10 ⁻⁰³	5.56 x 10 ⁻⁰⁴

These estimates consider a worst case for several reasons:

- For the calculation from concentrations monitored during the occupational monitoring campaign, the maximum concentration measured close to a source was used and assumed to exist over 24 h. In addition, 50 such sources were assumed to exist at a given site. While this figure is arbitrary, we consider it a worst case assumption, since more than half of all measurements even close to sources were below the LoQ of the occupational monitoring campaign.
- For the calculation of emissions with dust, the maximum dust emission given in the IPPC reference document (EC, 2007) was used.
- For this calculation, the mean of maximum Cr(VI) concentrations reported across all sodium chromate producing companies was used and this Cr(VI) concentration in sodium chlorate was assumed to also exist in dust from chlorate drying (conservative approach as not applicable for this applicant).
- With these release factors, EUSES models a concentration in air 100 m from the source of exposure (i.e. the sodium chlorate unit). At the sites of the sodium chlorate consortium, nobody is living so close to the chlorate unit.

Nevertheless, the estimate was not further refined by calculating the decrease of air concentrations in the vicinity of the plant as this would require full dispersion modelling. Such an approach is dependent on the

specific dispersion modelling software employed and would require extensive information for each site (including e.g. long-term meteorological data). In the present case, the results obtained from such dispersion modelling could not be validated with monitoring data since the limit of detection/quantification is well above the modelled values for the sites assessed here (see discussion above). In the light of these considerations, no further dispersion modelling was undertaken. Even with the worst case EUSES estimate, the exposure and the corresponding risks are very low (see below, $< 1 \times 10^{-6}$).

For oral exposure of humans via the environment, only exposure via drinking water and fish is considered. As explained in section 9.0.2.2., this approach is in agreement with the one chosen in the EU Risk Assessment Report for hexavalent chromium (ECB, 2005) and is supported by the data reported by EFSA (2014).

Table 13. Modelled exposure for humans via the environment: oral (drinking water and fish)

Pathway	Site A	Site B	Site C	Site E
Regional assessment				
Drinking water [ng/kg x d]	0.141	0.0945	0.0374	0.00480
Fish [ng/kg x d]	0.00421	0.00281	0.00112	0.000276
Sum of drinking water and fish [ng/kg x d]	0.145	0.0973	0.0385	0.00508
Local assessment				
Drinking water [ng/kg x d]	1.16	0.0881	0.731	0.330
Fish [ng/kg x d]	0.0663	0.00504	0.0421	0.0190
Sum of drinking water and fish [ng/kg x d]	1.22	0.0932	0.773	0.349

All values rounded to three significant figures for presentation, but unrounded values were used for calculation of sums

Note that for site B, the exposure via drinking water in the regional assessment is higher than the one in the local assessment. This is due to the fact that drinking water from surface water is assumed in the local assessment, while drinking water in groundwater is assumed in the regional assessment (see below).

Exposure via drinking water and fish calculated for the applicant's site E (SCB) is lower by approximately one order of magnitude at the regional scale. This is due to the fact that site E is known to be the only sodium chlorate (actually sodium chlorite) producing site within the region. Therefore, no second site is covered in the corresponding regional assessment using EUSES as was the case for sites A to C. With regard to the local assessment, exposure via drinking water and fish calculated for the applicant's site E (SCB) is lower compared to sites A and C and but higher in relation to site B. Site E is therefore well within the range calculated from sites A to C for the earlier AfA (2015) representative for the consortium. It must be noted that the release factor to water applied for site E is based on the LOQ for Cr(VI) of 50 µg/L ($\frac{1}{2}$ LOQ assumed) and due to quantitative reductive treatment of waste water will actually be much lower. But even under the completely unrealistic assumption that waste water concentration would equal the LOQ (release factor to water 2.758% instead of 1.379%) the resulting values for local intake via drinking water and fish are still within the range given by sites A to C (0.659 and 0.0379 mg/kg x d for drinking water and fish, respectively).

In all these cases, the overall exposure is dominated by the drinking water pathway. For the local concentration in drinking water, EUSES takes the local PEC in surface water as the basis, directly equating it with the concentration in drinking water in the present case. In this context, the estimated values are unrealistic for the following reasons:

- The approach chosen will likely “*over-estimate the actual indirect exposure as conversion of Cr (VI) to Cr (III) is expected to occur under the vast majority of environmental conditions*” (ECB, 2005). This reduction is not considered in the calculated exposure values presented above.
- EUSES typically specifies a “purification factor” that accounts for removal processes from surface water in deriving the concentration in drinking water, e.g. by evaporation or adsorption to suspended solids. The latter, however, is estimated by log Kow rather than by any specific partition coefficients. This approach is not feasible for inorganics and therefore the estimate does not account for adsorption to suspended particles as a removal process before and during drinking water purification. While this impact is difficult to quantify, the value of 50% (i.e. reduction by a factor of 2) for adsorption onto sewage sludge as applied in the EU RAR (see section 9.0.2.2) can serve as an indication of the degree of Cr(VI) adsorption onto suspended solids in surface water.
- The PEC in surface water is calculated for the mixing zone, neglecting the fact that for drinking water preparation additional water sources are added.

- Overall, the conservatism of EUSES in relation to exposure via drinking water is rated as “worst case” by the developers of the software (RIVM, 2004).

In the light of these substance-specific and model-inherent considerations, the estimate for local exposure via drinking water is considered unrealistic. The impact of all of these issues is impossible to quantify, but an overall reduction of the local Cr(VI) concentration in drinking water calculated in EUSES due to the factors above by a factor of 5 seems to be reasonable in the light of a factor of 2 due to removal by adsorption alone. The regional exposure via drinking water is based on the PEC in groundwater (because the regional PEC in surface water is lower). The Cr(VI) concentration in groundwater is taken directly from the pore water concentration in soil, which in turn is modelled from the Cr(VI) concentration in soil. Cr(VI) reduction in soil is a well-known process and the EU Risk Assessment Report states that “chromium (VI) is reduced to chromium (III) by organic matter and this process occurs reasonably readily in soils” and assumes “chromium present in soil following application is in the form of chromium (III)” (ECB, 2005). In addition, deposition (the main pathway of groundwater contamination relevant here) is calculated in EUSES for a circle around the source with a radius of 1000 m (RIVM, 2004) so that the resulting groundwater concentration is also valid only for the groundwater below this area. Similar to the local drinking water concentration discussed above, any additional dilution with other groundwater or surface water for drinking water purposes is not considered. Modelled groundwater concentrations of Cr(VI) (and drinking water concentrations derived from them) are therefore also considered unrealistic. A reduction of the regional drinking water concentration by a factor of 5 is therefore used in the assessment.

The reduction of local and regional exposure via drinking water by a factor of 5 is somewhat arbitrary. However, given the many factors pointing towards an overestimation in these values, the reduction is considered to still represent a conservative estimate.

Local exposure via fish consumption and inhalation are used together with this regional exposure via drinking water in the aggregated risk characterisation for the use covered by this CSR. For the intake via consumption of fish, the local scale also represents a (probably unrealistic) worst case situation. Most of the arguments presented above for the drinking water (from surface water) pathway are also valid in relation to the consumption of fish. However, the argument that other waters are added for the preparation of drinking water is specific to the drinking water pathway and is not relevant for fish. In a conservative estimate, the local contribution of fish consumption is therefore retained in the risk estimate. It must be noted, however, that “(p)eople do not consume 100% of their food products from the immediate vicinity of a point source. Therefore, the local assessment represents a situation which does not exist in reality” (ECHA, 2016).

A comparison of these modelled exposure estimates with the exposure-risk relationships (ERR) derived by ECHA (2013) for the general population (see Section 9.0.3) results in the risk estimates shown in the following tables for the regional and the local assessment.

Table 14. Risk estimates for humans via the environment (general population, local assessment)

Pathway	Site A	Site B	Site C	Site E
Inhalation	8.29×10^{-08}	4.87×10^{-08}	1.70×10^{-07}	1.61×10^{-08}
Drinking water *	1.85×10^{-07}	1.41×10^{-08}	1.17×10^{-08}	5.28×10^{-08}
Fish	5.30×10^{-08}	4.03×10^{-09}	3.37×10^{-08}	1.52×10^{-08}
Aggregated for all pathways	3.21×10^{-07}	6.68×10^{-08}	3.21×10^{-07}	8.41×10^{-08}
Contribution drinking water	58%	21%	36%	63%
Contribution inhalation	26%	73%	53%	19%

All values rounded to three significant figures for presentation, but unrounded values were used for calculation of sums

*: calculation performed using 1/5 of the exposure given in Table 13; for justification see above

Table 15. Risk estimates for humans via the environment (general population, regional assessment)

Pathway	Site A	Site B	Site C	Site E
Inhalation	1.38×10^{-18}	1.02×10^{-18}	2.15×10^{-18}	1.58×10^{-19}
Drinking water *	2.25×10^{-08}	1.51×10^{-08}	5.98×10^{-09}	7.69×10^{-10}
Fish	3.37×10^{-09}	2.25×10^{-09}	8.92×10^{-10}	2.20×10^{-10}
Aggregated for all pathways	2.59×10^{-08}	1.74×10^{-08}	6.87×10^{-09}	9.89×10^{-10}
Contribution drinking water	87%	87%	87%	77.71%
Contribution inhalation	<0.0001%	<0.0001%	<0.0001%	<0.0001%

All values rounded to three significant figures for presentation, but unrounded values were used for calculation of sums

*: calculation performed using 1/5 of the exposure given in Table 13; for justification see above

For all four sites, the pathway-specific estimated risks as well as the aggregated estimated risk (all pathways combined) are below the risk level⁷ of 1×10^{-6} for the general population, at least by a factor of 3.

The risk estimates for the three sites A to C cover the two sites using the highest amount of SD. In addition, the risk estimates for all four sites show that – while the aggregated values are similar – some variety of potential exposure patterns is covered, with the local contribution from drinking water ranging between 21-63% and the one from air ranging between 19-73% in the local assessment. The applicant's site E is characterized by the lowest contribution from air due to the process-inherent lower emission (no drying of sodium chlorate). Correspondingly, contribution of drinking water is higher compared to sites A to C. For the regional assessment, drinking water is the dominant pathway with negligible exposure via inhalation.

The exposure estimates forming the basis of the risk estimates must be put into perspective. The following discussion is based on the Cr(VI) concentrations originally calculated in EUSES, i.e. without the reduction by a factor of 5 used in the risk assessment. The Cr(VI) concentration calculated for regional drinking water range between 1.3-4.4 ng/L for sites A to C and amounts to 0.168 ng/L for the applicant's site E. These values are very low and are about two orders of magnitude lower than the Cr(VI) concentration in drinking water (270 ng/L) corresponding to a risk of 1×10^{-6} according to an estimate derived for the German Federal Environmental Agency (Roller, 2012). Even the local drinking water concentrations modelled for sites A-C (3.1-40 ng Cr(VI)/L) as well as the one for site E (11.6 ng Cr(VI)/L) are about 1-2 orders of magnitude below this level. It is noted that the estimate by Roller (2012) is almost seven-fold lower than the one derived by ECHA (2013) for the general population that is based on a draft US EPA report.

With the site-specific fractions of Cr(VI) out of total Cr measured in the effluent at the three sites A to C, the total Cr concentration in regional drinking water corresponds to 1.8-71 ng/L. These values are 3-4 orders of magnitude lower than the standard set in EU Directive 98/83/EC on the quality of water intended for human consumption (total Cr: 50 000 ng/L). Even the local concentrations of total chromium in drinking water for sites A to C (considered unrealistic as discussed above) are lower than this standard by 2-4 orders of magnitude (7.7-650 ng/L).

They are also towards the lower end of background concentrations reported in the FOREGS-EuroGeoSurveys Geochemical Baseline Database⁷ for total Cr in stream waters (AM: 790 ng/L, Median: 380 ng/L, range: 5-43 000 ng/L, n=804).

These data show that even at the local scale, Cr(VI) releases from the use covered by this CSR lead to low concentrations in the environment and are fully in line with national and international legislation, also in respect to drinking water quality (limit value: 50 µg/L total chromium).

Overall, these considerations show that the risks for humans exposed via the environment are low, even when conservative assumptions are used in modelling approaches. The exposure estimates presented here are very conservative for the situation of this applicant as the applicant performs reductive treatment of waste water, leading to quantitative reduction of Cr(VI) to Cr(III). The release factor to water applied for the estimate is based on ½ LoQ for Cr(VI) because all monitoring values for waste water confirmed Cr(VI) concentration below the LoQ (non-detects). Exposure via waste water is the most important pathway for site E (SCB) because of the low emission to air (no drying of sodium chlorate).

For the SEA specific for this AfA, the risk estimate calculated for site E was used for further analysis.

For the sake of completeness, risk characterisation ratios have also been calculated for the oral and inhalation route based on the oral and inhalation DNELs for systemic effects after long-term exposure (see section 9.0.3). The RCRs in the following table document that the exposure is far below the DNELs resulting in very, very low RCRs (several orders of magnitude below 1), which indicate that there is no risk for effects on fertility under the calculated exposure of humans via the environment.

⁷ <http://weppi.gtk.fi/publ/foregsatlas/ForegsData.php>

Table 16. RCRs for humans via the environment

Pathway	Site A	Site B	Site C	Site E
Regional assessment				
Oral exposure [ng/kg x d]	0.145	0.0973	0.0385	0.00508
DNEL oral systemic long-term	17 µg/kg x d			
RCR oral	8.5 x 10E-6	5.7 x 10E-6	2.3 x 10E-6	3 x 10E-7
Inhalation exposure [ng/m ³]	4.76 x 10 ⁻¹⁴	3.53 x 10 ⁻¹⁴	7.42 x 10 ⁻¹⁴	5.44 x 10 ⁻¹⁵
DNEL inhalation systemic long-term	11 µg/m ³			
RCR inhalation	4 x 10E-18	3 x 10E-18	7 x 10E-18	0.5 x 10E-18
Local assessment				
Oral exposure [ng/kg x d]	1.22	0.0932	0.773	0.349
DNEL oral systemic long-term	17 µg/kg x d			
RCR oral	7.2 x 10E-5	0.6 x 10E-5	4.6 x 10E-5	2.1 x 10E-5
Inhalation exposure [ng/m ³]	2.86 x 10 ⁻⁰³	1.68 x 10 ⁻⁰³	5.88 x 10 ⁻⁰³	5.56 x 10 ⁻⁰⁴
DNEL inhalation systemic long-term	11 µg/m ³			
RCR inhalation	3 x 10E-7	2 x 10E-7	5 x 10E-7	0.5 x 10E-7

9.1.2. Worker contributing scenario 1: T1: Feeding SD solution into the process (PROC 8b)

9.1.2.1. Conditions of use

Feeding of the SD solution into the process is essentially a closed process. A potential exposure exists during coupling/de-coupling of hoses.

	Method
Product (article) characteristics	
• Concentration of substance in mixture: = 28% <i>Concentration of Cr(VI) based on SD concentration of 70%.</i>	External Tool (ART 1.5)
• Product type: Powders dissolved in a liquid or incorporated in a liquid matrix	External Tool (ART 1.5)
• Viscosity: Liquids with low viscosity (like water)	External Tool (ART 1.5)
Amount used (or contained in articles), frequency and duration of use/exposure	
• Duration of activity: 30 minutes <i>Maximum duration for connection/disconnecting from survey of companies: 30 minutes/day (on days of task being performed)</i>	External Tool (ART 1.5)
• Frequency of use/task: = 24 days per year <i>Maximum value from survey of companies</i>	External Tool (ART 1.5)
Technical and organisational conditions and measures	
• Place of use: Indoors - 1000 m ³	External Tool (ART 1.5)
• Ventilation rate of general ventilation system: 10 ACH	External Tool (ART 1.5)
Conditions and measures related to personal protection, hygiene and health evaluation	
• Surface contamination/fugitive emission sources: The process is not fully enclosed and the integrity of that enclosure is not regularly monitored, but effective housekeeping practices are in place.	External Tool (ART 1.5)
• Protective apron	
• Wear chemically resistant gloves (tested to EN374) in combination with specific activity training.	
• Respiratory Protection: Yes (Respirator with APF of 20) [Effectiveness Inhal: 95%]	External Tool (ART 1.5)
Other conditions affecting workers exposure	
• Primary emission source proximity: The primary emission source is located in the breathing zone of the worker (near field, < 1 m)	External Tool (ART 1.5)
• Activity class and subclass: Handling of contaminated objects	External Tool (ART 1.5)
• Handling of contaminated objects (size of object): Activities with treated/contaminated objects (surface < 0.1 m ²)	External Tool (ART 1.5)
• Handling of contaminated objects (degree of contamination): < 10% of surface	External Tool (ART 1.5)

9.1.2.2. Exposure for workers

Air monitoring results

Since this task is very infrequent, only two monitoring results from the same site are available. Monitoring was performed on two consecutive days by the same worker to obtain two values (under normal work routine, this task is performed on one day). The monitoring results are shown in the following table.

Table 17. Monitored exposure for workers: task 1

No. of sites covered	No. of measurements	Measurements <LoQ	Frequency (d/a)	Duration [min/shift]	Inhalation exposure [ng/m ³]	
					Monitoring result	Long-term TWA
1	2	100%	24	30	1.2* (without RPE)	
1	2	100%	24	30	0.06** (with RPE)	0.000375**

All calculated values (TWA, long-term) rounded to two significant figures for presentation, but unrounded values used for calculation of exposure; * Both values were below the limit of quantification (LoQ: 2.4 ng/m³) and taken here as one half the LoQ; ** includes reduction by 95% due to respiratory protection (half mask with P3 filter or full mask with P3 filter or P3 combination filter).

Both monitoring results were below the limit of quantification (LoQ). This finding is remarkable, since on day 1 there was some spill of sodium dichromate (about 100 mL), most probably because the worker was hindered by the monitoring device from carrying out the task in his normal routine (see Figure A4-3 in Annex 4).

While monitoring results are somewhat limited by the fact that personal monitoring could not be performed (see section 9.0.2.3), this finding gives some indication that exposure is low even when handling the concentrated SD solution in this task. Our interpretation is that SD dissolved in water is not available for inhalation exposure if no aerosols are generated.

Modelling results

The modelled exposure estimates are shown in the following table.

Table 18. Modelled Exposure for Workers: task 1

Frequency (d/a)	Duration [min/shift]	Inhalation exposure [ng/m ³]		
		Task-based	TWA (on day of exposure)	Long-term TWA
24	30	810 (without RPE)		
24	30	41 (with RPE)*	2.5*	0.25*

All calculated values (TWA, long-term) rounded to two significant figures for presentation, but unrounded values used for calculation of exposure; full ART reports are attached in Annex 5; * includes reduction by 95% due to respiratory protection (half mask with P3 filter or full mask with P3 filter or P3 combination filter)

The modelled exposure estimate is based on (also see section 9.0.2.3):

- the maximum SD concentration of 70% (28% Cr(VI)), while the median across all companies is 61% (range: 60-70%)
- an exposure duration of 30 minutes; while this represents the median across all companies (range: 2-120 minutes), the durations given in the survey largely represent the entire task duration (for pumping the SD solution into the system), rather than the duration for tasks relevant for exposure (i.e. connecting/disconnecting pipes/pumps); the actual transfer is in a closed system
- the highest frequency reported in the survey that is four times higher than the median (6 times/year, range: 0.5-24 times/year).

As a consequence, the long-term inhalation estimate represents an upper end not existing in reality, because companies using the solution with the highest SD concentration are not the ones with the highest use frequencies. The following input for the activity emission potential within ART have been selected:

- Activities with treated/contaminated objects (surface <0.1 m²)
- Contamination < 10% surface

These were chosen to reflect handling of the concentrated SD solution, which is not only carcinogenic, but also corrosive to skin and skin sensitising (see section 9.0.2.3). Special care is therefore taken to prevent contamination during the connection/disconnection of pipes/pumps, with 30 cm x 30 cm (0.09 m²) showing little contamination (<10%), the latter considered to reflect real conditions.

Based on the experience from the Caffaro Brescia site and due to technological improvements it is currently envisaged, that task 1 will probably be performed only 6 times a year at the SCB Bussi site, i.e. 4 times less than assumed in the modelling, with a similar duration of 30 minutes. On basis of a modelled task based value 810 ng/m^3 , and under consideration of respiratory protection with 95% reduction this would result in a long-term **TWA of 0.06 ng/m^3** , i.e. four times lower than calculated in the former CSR. This value will be used for comparison of the predicted exposure estimate at the SCB site in Bussi sul Tirino in comparison to the former estimate for the Caffaro Brescia site. It should be noted that the feeding solution in Bussi will also have a lower concentration (67%) than the 70% assumed for the modelling, however the influence of this lower concentration on the overall estimate is marginal and not further quantified.

Discussion and conclusions

In summary, monitored and modelled long-term inhalation exposure to Cr(VI) was estimated to be:

- Monitoring: 0.00038 ng/m^3 (n=2, limited coverage)
- ART modelling: 0.25 ng/m^3 (worst case)

Due to the limited coverage of the monitoring data, the long-term TWA of the modelling result (0.25 ng/m^3) was used in the former CSR for aggregated exposure assessment and risk characterisation (see section 9.1.6). The exposure estimate (0.06 ng/m^3) under consideration of the future situation at the SCB Bussi plant will be used in this CSR for risk characterisation.

Note that respiratory protection was chosen in ART modelling performed after the monitoring campaign on the basis of initial modelling results. Therefore, the worker performing this task during the monitoring campaign did not wear respiratory protection (see Figure A4-3 in Annex 4). The limited monitoring data, however, suggest that this is a precautionary measure which will also be applied in the future SCB plant.

Final exposure estimate for task 1: 0.06 ng/m^3

9.1.3. Worker contributing scenario 2: T2: Use in closed batch process: Sampling of the electrolyte solution (PROC 3)

9.1.3.1. Conditions of use

Sampling of the electrolyte solution in sodium chlorate production unit

	Method
Product (article) characteristics	
• Concentration of substance in mixture: = 0.184% <i>Concentration of Cr(VI) based on SD concentration of 6.5 g/L in the electrolyte and a density of the electrolyte of 1400 g/L.</i>	External Tool (ART 1.5)
• Product type: Powders dissolved in a liquid or incorporated in a liquid matrix	External Tool (ART 1.5)
• Viscosity: Liquids with low viscosity (like water)	External Tool (ART 1.5)
Amount used (or contained in articles), frequency and duration of use/exposure	
• Duration of activity: 30 min <i>Maximum duration for sampling from survey of companies: 30 minutes/day</i>	External Tool (ART 1.5)

	Method
• Frequency of use/task: = 240 days per year	External Tool (ART 1.5)
Technical and organisational conditions and measures	
• Place of use: Indoors - 1000 m ³	External Tool (ART 1.5)
• Ventilation rate of general ventilation system: 10 ACH	External Tool (ART 1.5)
Conditions and measures related to personal protection, hygiene and health evaluation	
• Surface contamination/fugitive emission sources: The process is not fully enclosed and the integrity of that enclosure is not regularly monitored, but effective housekeeping practices are in place.	External Tool (ART 1.5)
• Wear chemically resistant gloves (tested to EN374) in combination with specific activity training.	
Other conditions affecting workers exposure	
• Primary emission source proximity: The primary emission source is located in the breathing zone of the worker (near field, < 1 m)	External Tool (ART 1.5)
• Activity class and subclass: Transfer of liquid products - falling liquid	External Tool (ART 1.5)
• Falling liquid (transfer rate): 0.1 - 1 L/min	External Tool (ART 1.5)
• Containment of the process: Handling that reduces contact between product and adjacent air	External Tool (ART 1.5)
• Transfer Loading Type : Submerged loading, where the liquid dispenser remains below the fluid level reducing the amount of aerosol formation	External Tool (ART 1.5)

9.1.3.2. Exposure and risks for workers

Air monitoring results

Sampling is a daily task at all sites and a total of 35 monitoring values were obtained from all 8 sites included in the monitoring campaign. The descriptive statistics for the entire set is included in Annex 3A and shows that a few very high values dominate the distribution. These are identified as outliers by the statistical software (see Annex 3A for details) and the maximum value is about 25-times higher than the 90th percentile. In fact, the impact is so dominant that the arithmetic mean (32.7 ng/m³) is higher than the 90th percentile (30.0 ng/m³). Results from the same monitoring points giving the two highest values on one day were considerably lower on the other monitoring day (18.9 vs. 767.8 ng/m³ and 8.2 vs. 129.5 ng/m³). These two high values are from two different sites of different companies and relate to tasks for which the procedure was changed after the monitoring campaign in the light of the comparatively high exposure monitored:

- 767.8 ng/m³: cleaning of a sampling point with a water hose after taking the samples under a condition with open access to the electrolyte, a procedure potentially associated with aerosol generation; this has technically been changed by enclosing the electrolyte.
- 129.5 ng/m³: the sampling procedure involves returning the samples into the process, which is performed by emptying a bucket with sampled solution into an open receiving container. This container showed salt crystals potentially containing SD at its borders (see Figure A4-10 in Annex 4), which were considered to be the source of the elevated Cr(VI) concentrations monitored. The process was changed to include a lid on the receiving container (see Figure A4-11 in Annex 4). This change is believed to result in considerably lower exposure levels at this process point.

Since the tasks are no longer performed in the way existing during the monitoring campaign, all values related these two monitoring points (four monitoring results from two sites) are excluded from further analyses. The descriptive statistics for the remaining set (n=31) is included in Annex 3A. While the statistical software still identifies the maximum values as outliers, the maximum of 49.9 ng/m³ is only about 2-times higher than the 90th percentile. In addition, the arithmetic mean (7.1 ng/m³) is clearly lower than the 90th percentile (23 ng/m³). The following table shows the inhalation exposure estimate based on the 90th percentile of the monitoring results.

Table 19. Monitored exposure for workers: task 2

No. of sites covered	No. of measurements	Measurements <LoQ	Frequency (d/a)	Duration [min/shift]	Inhalation exposure [ng/m ³]	
					Monitoring result*	Long-term TWA
8	31	58%	240	30	23**	1.4

All calculated values (TWA, long-term) rounded to two significant figures for presentation, but unrounded values used for calculation of exposure; * calculated 90th percentiles (values <LoQ included with one half of the LoQ (i.e. 1.2 ng/m³)); ** excluding four values (767.8 and 18.9 ng/m³ at one site, 129.5 ng/m³ and 8.2 ng/m³ at the other site; see text for details).

More than half of the monitoring results from all 8 sites included in the monitoring campaign are below the limit of quantification (LoQ). Monitoring points with results below the LoQ not only cover task 2 sampling points with some form of containment (see e.g. Figures A4-5 and A4-9 in Annex 4), but also uncontained sampling points (see e.g. Figures A4-6 and A4-7 in Annex 4). Higher values also did not appear to be related to the number of samples or the volume of samples taken. For example, at one monitoring point (formally assigned to task 3, since simple pH measurements are performed) both measurements were <LoQ, although 24 samples are processed per shift and manually emptied into a bucket from a jug (see Figure A4-15 in Annex 4).

Our interpretation is that the monitored concentrations reflect rather the degree of salt crystal presence at or around sampling points than the level of containment or the volume of samples taken. Small amounts of liquid remain on the sampling outlets or in collecting pans below these outlets, crystallise and dry out over time (see e.g. Figure A4-8 in Annex 4). In one case, a sampling procedure led to small spills of the electrolyte solution on the floor that dried out over time, potentially resulting in higher Cr(VI) concentrations. Note, however, that this finding is an artefact since cleaning the floor with a water hose (which is typically performed) was impossible during the monitoring campaign for safety reasons due to electricity supplies for the monitoring pumps lying on the floor (the sampling procedure causing these spills is currently under review).

In support of this interpretation, the visual impression of the degree of such salt crystal presence (easily identifiable by a yellowish colour) by experienced air monitoring personnel and consultants during the monitoring campaign was in agreement with elevated monitoring values. In addition, the site where dried out spills on the floor were observed was also the only site where all monitoring values for task 2 and task 3 (see section 9.1.4) were consistently above the limit of quantification. However, the monitored dust and Cr(VI) concentrations for task 2 are not extreme (inhalable dust: 0.060-0.068 mg/m³; Cr(VI): 11-24 ng/m³; also see Figure 1).

There is some relationship between the concentrations of airborne (inhalable) dust concentrations and the concentrations of Cr(VI), as shown in the Figure 1 (note that this figure also includes the two highest values excluded from the derivation of the exposure estimate).

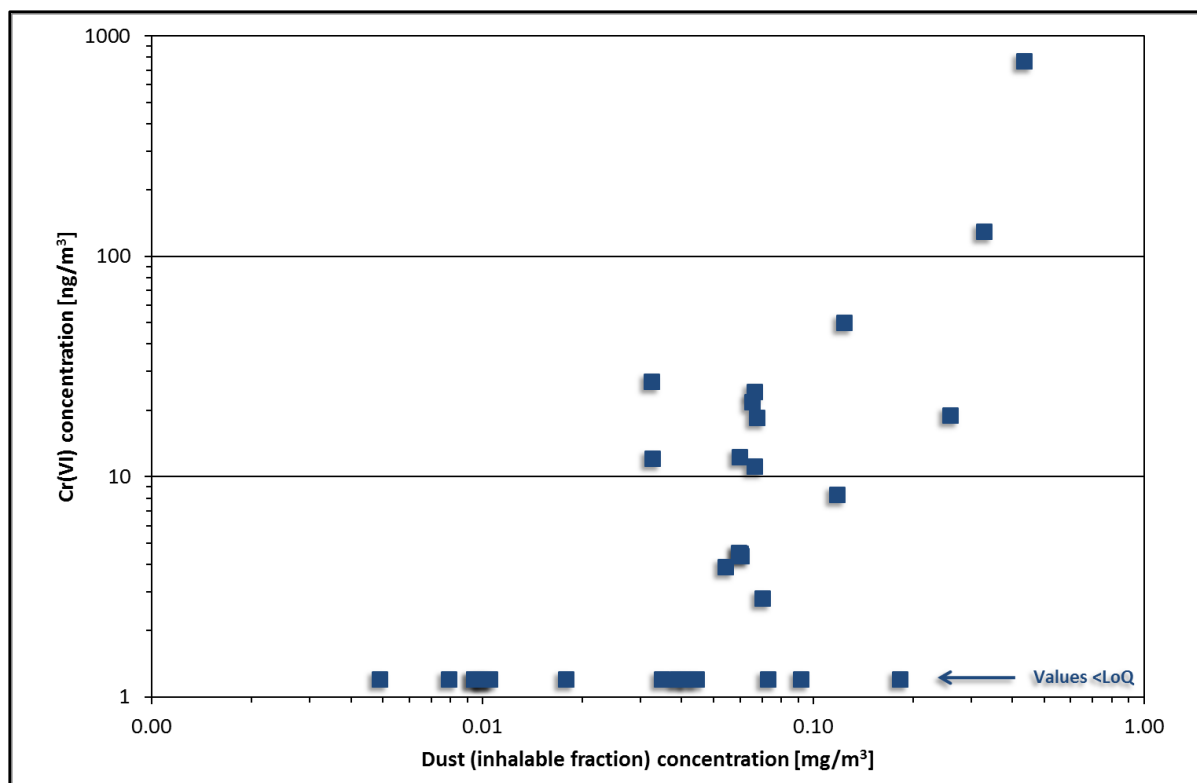


Figure 1 Correlation between dust and Cr(VI) concentrations for task 2 (sampling)

Overall, the monitoring results provide evidence that the higher exposures represented by the 90th percentile are more a consequence of drying out of salt crystals containing SD than from aerosol exposure due to handling SD dissolved in the electrolyte solution. As a consequence, the type of containment of sampling outlets as well as the volume of samples is not considered decisive for the resulting exposure.

Modelling results

The modelled exposure estimates are shown in the following table.

Table 20. Modelled exposure for workers: task 2

Frequency (d/a)	Duration [min/shift]	Inhalation exposure [ng/m ³]		
		Task-based	TWA (on day of exposure)	Long-term TWA
240	30	16	1.0	1.0

All calculated values (TWA, long-term) rounded to two significant figures for presentation, but unrounded values used for calculation of exposure; full ART reports are attached in Annex.

The modelled exposure estimate is based on (also see section 9.0.2.3):

- the maximum SD concentration of 0.464% (0.184% Cr(VI))
- a maximum exposure duration of 30 minutes; range: 12-30 minutes
- the highest frequency reported in the survey (each shift), which is realistic for sampling

As a consequence, the long-term inhalation estimate represents an upper end not existing in reality, because the company reporting the maximum concentration also reported a task duration for sampling and production lab analyses together (T2 and T3) of 30 minutes. Therefore, the containment level and loading type were not set to worst case conditions, although such conditions (“handling that reduces contact between product and adjacent air” and “submerged loading”) were not present at all sites (also see discussion in section 9.0.2.3 above). The monitoring results suggest that these conditions of taking the samples are not decisive, as long as aerosol formation (e.g. from hosing the sampling point) or other processes associated with an increasing potential for SD to become airborne (e.g. from dried out electrolyte solution containing SD) are prevented.

It is currently envisaged, that task 2 will only be performed 2 times per shift at the SCB Bussi site. One sample has to be taken during sodium chlorate production and one sample during sodium chlorite production per shift. Every sampling takes ca. 10 minutes so that the duration per shift of this activity will probably decrease from 30 minutes (assumption for former Caffaro Brescia CSR) to 20 minutes (SCB Bussi site). On basis of the monitoring value of 23 ng/m³ and the future reduced duration of the activity a long-term **TWA of 0.96 ng/m³** (i.e. about 1.5 times lower than calculated in the former CSR) would result. This value will be used for a comparison of the predicted exposure estimate at the SCB site in Bussi sul Tirino in comparison to the former monitoring based TWA long-term used for the Caffaro Brescia site. Taking into consideration that the SD concentration in the brine will probably also be lower ($\leq 5\%$ instead of 6.5% as assumed in the former CSR) will additionally reduce the exposure concentration during task 2 in the SCB plant. However, this additional reduction is not considered quantitatively in the comparison, but underlines the conservatism of the calculation based on the former monitoring campaign.

Discussion and conclusions

In summary, monitored and modelled long-term inhalation exposure to Cr(VI) was estimated to be:

- Monitoring: 1.4 ng/m³ (n=33, 90th percentile from 8 sites)
- ART modelling: 1.0 ng/m³ (worst case)

The estimates for long-term inhalation exposure derived from monitoring data and higher tier modelling agree very well. The monitoring data were obtained by static sampling (necessary to obtain a sufficiently low LoQ, see section 9.0.2.3). Therefore, the monitoring data are somewhat uncertain in relation to actual exposure in the breathing zone of workers. In contrast to “classic” stationary sampling, however, which is typically designed to monitor exposure in the general work area, stationary sampling during the monitoring campaign was performed close to the potential sources of exposure for task 2 (i.e. sampling outlets) and the location of the worker during the task. The fact that the worst case ART modelling result is actually slightly lower than the monitoring data demonstrates that the strategy of the monitoring campaign reflects actual inhalation exposure.

Due to the extensive coverage of the monitoring data, the long-term TWA based on the 90th percentile of the monitoring data (1.4 ng/m³) has been used in the former aggregated exposure assessment and risk characterisation (see section 9.1.6). The exposure estimate under consideration of the future situation at the SCB Bussi plant (0.96 ng/m³) will be used in this CSR for risk characterisation.

Final exposure estimate for task 2: 0.96 ng/m³

9.1.4. Worker contributing scenario 3: T3: Production lab analyses (PROC 15)

9.1.4.1. Conditions of use

Lab analyses of the electrolyte solution without LEV in sodium chlorate production unit

	Method
Product (article) characteristics	
<ul style="list-style-type: none"> • Concentration of substance in mixture: = 0.092% <i>Concentration of Cr(VI) based on SD concentration of 6.5 g/L in the electrolyte and a density of the electrolyte of 1400 g/L. The resulting concentration of 0.184% was divided by 2 (0.092%) since the sampled solution is rapidly diluted with</i>	External Tool (ART 1.5)

	Method
<i>reagents for the analyses to be performed.</i>	
• Product type: Powders dissolved in a liquid or incorporated in a liquid matrix	External Tool (ART 1.5)
• Viscosity: Liquids with low viscosity (like water)	External Tool (ART 1.5)
Amount used (or contained in articles), frequency and duration of use/exposure	
• Duration of activity: 30 minutes <i>Maximum duration for analyses in the production lab (not present at all sites) from survey of companies: 30 minutes/day</i>	External Tool (ART 1.5)
• Frequency of use/task: = 240 days per year	External Tool (ART 1.5)
Technical and organisational conditions and measures	
• Place of use: Indoors - any size workroom	External Tool (ART 1.5)
• Ventilation rate of general ventilation system: 3 ACH	External Tool (ART 1.5)
Conditions and measures related to personal protection, hygiene and health evaluation	
• Surface contamination/fugitive emission sources: The process is not fully enclosed and the integrity of that enclosure is not regularly monitored, but effective housekeeping practices are in place.	External Tool (ART 1.5)
• Wear chemically resistant gloves (tested to EN374) in combination with specific activity training.	
Other conditions affecting workers exposure	
• Primary emission source proximity: The primary emission source is located in the breathing zone of the worker (near field, < 1 m)	External Tool (ART 1.5)
• Activity class and subclass: Transfer of liquid products - falling liquid	External Tool (ART 1.5)
• Falling liquid (transfer rate): 0.1 - 1 L/min	External Tool (ART 1.5)
• Containment of the process: Handling that reduces contact between product and adjacent air	External Tool (ART 1.5)
• Transfer Loading Type: Submerged loading, where the liquid dispenser remains below the fluid level reducing the amount of aerosol formation	External Tool (ART 1.5)

9.1.4.2. Exposure and risks for workers

Air monitoring results

Analyses in the production lab are a daily task at all sites and a total of 18 monitoring values were obtained from all 8 sites included in the monitoring campaign. The full descriptive statistics for the entire set is included in Annex 3A. The following table shows the inhalation exposure estimate based on the 90th percentile of the monitoring results.

Table 21. Monitored exposure for workers: task 3

No. of sites covered	No. of measurements	Measurements <LoQ	Frequency (d/a)	Duration [min/shift]	Inhalation exposure [ng/m ³]	
					Monitoring result*	Long-term TWA
8	18	78%	240	30	7.7	0.48

All calculated values (TWA, long-term) rounded to two significant figures for presentation, but unrounded values used for calculation of exposure; * calculated 90th percentiles (values <LoQ included with one half of the LoQ (i.e. 1.2 ng/m³)).

More than three quarters of the monitoring results from all 8 sites included in the monitoring campaign are below the limit of quantification (LoQ), i.e. there are only 4 monitoring results above the LoQ (3.4-9.8 ng/m³, see Annex 3A). Two of these relate to sampling points, for which the Cr(VI) concentration on the other monitoring day was below the limit of quantification, i.e. there was only one monitoring point in one production

lab for which the Cr(VI) concentration was consistently above the LoQ on both monitoring days (7.8 and 7.3 ng/m³, respectively). These results relate to the site, where small dried out spills of the electrolyte solution on the floor close to sampling outlets were observed (see section 9.1.3.2). Although limited by the small number of results, our interpretation is that the monitoring results in the production lab are largely determined by cross-contamination from the sampling procedure rather than resulting from production lab analyses as such (note that the sampling procedure is currently under review and that the drying out of crystals was due to the monitoring campaign, see section 9.1.3.2 for details).

As a result of the high number of non-detects (evaluated with one half of the LoQ) the statistical software identifies most of the quantifiable Cr(VI) concentrations as outliers. However, all values were retained for the derivation of the 90th percentile since the overall exposure level is considered to be representative for the exposure levels during this task, expressing e.g. between worker variability at monitoring points where one value was below the LoQ on one day and above the LoQ on the next day.

Modelling results

The modelled exposure estimates are shown in the following table.

Table 22. Modelled exposure for workers: task 3

Frequency (d/a)	Duration [min/shift]	Inhalation exposure [ng/m ³]		
		Task-based	TWA (on day of exposure)	Long-term TWA
240	30	14	0.88	0.88

All calculated values (TWA, long-term) rounded to two significant figures for presentation, but unrounded values used for calculation of exposure; full ART reports are attached in Annex 5.

The modelled exposure estimates are based on (also see section 9.0.2.3):

- the maximum SD concentration of 0.464% (0.184% Cr(VI)), divided by 2 to account for rapid dilution during laboratory analysis (this dilution factor is also conservative)
- a maximum exposure duration of 30 minutes
- the highest frequency reported in the survey (daily), which is realistic for production lab analyses

As a consequence, the long-term inhalation estimate represents an upper end not existing in reality, because the company reporting the maximum concentration also reported a task duration for sampling and production lab analyses together (T2 and T3) of 30 minutes.

It is currently envisaged that the analysis of the samples in the production lab takes 30 minutes per sample, i.e. 60 minutes for both samples per shift, i.e. the duration is 2 times longer than assumed in the former Caffaro Brescia CSR. On basis of the monitoring value of 7.7 ng/m³ and taking into account a duration of 60 minutes per shift a long-term TWA of 0.96 ng/m³ results, i.e. 2 times higher than calculated in the former CSR would result. As the work in the SCB production site laboratory will be performed under an enclosing hood this value can be reduced by 10% (effectiveness of any enclosing hood) resulting in a **long-term TWA of 0.096 ng/m³**. This value will be used for a comparison of the predicted exposure estimate at the SCB site in Bussi sul Tirino in comparison to the former monitoring based TWA long-term used for the Caffaro Brescia site. Taking into consideration that the SD concentration in the brine will probably also be lower ($\leq 5\%$) instead of 6.5% as assumed in the former CSR will reduce the exposure concentration during task 2 in the SCB plant. Exposure is also reduced by the fact that the two samples taken during the day are analysed in the central lab. However, this additional reduction is not considered quantitatively in the comparison, but underlines the conservatism of the calculation. Assuming an effectiveness of the enclosing hood of only 10% is an additional conservative assessment which contributes to the fact that the final version of hood has not been determined. Probably and even much more effective hood will be installed.

Discussion and conclusions

In summary, monitored and modelled long-term inhalation exposure to Cr(VI) was estimated to be:

- Monitoring: 0.48 ng/m³ (n=18, 90th percentile from 8 sites)

- ART modelling: 0.88 ng/m³ (worst case)

The estimates for long-term inhalation exposure derived from monitoring data and higher tier modelling agree very well. The monitoring data were obtained by static sampling (necessary to obtain a sufficiently low LoQ, see section 9.0.2.3). Therefore, the monitoring data are somewhat uncertain in relation to actual exposure in the breathing zone of workers. In contrast to “classic” stationary sampling, however, which is typically designed to monitor exposure in the general work area, stationary sampling during the monitoring campaign was performed close to the potential sources of exposure for task 3 (i.e. workbenches in production labs) and the location of the worker during this task.

ART modelling results in somewhat higher estimates, but the difference to the monitoring data is small (less than a factor of 2). In addition, the modelling results largely reflect worst case conditions (as discussed above) and the transfer rate assumed in the modelling (0.1-1 L/min) is conservative (real transfer rates 0.02-0.5 L/min, median 0.02 L/min; see section 9.0.2.3). Furthermore, the dilution of the electrolyte solution during production lab analyses was chosen very conservatively with only twofold dilution, while in fact many analyses with the transfer of the samples involve pipetting small amounts (e.g. 5-10 mL) into larger volumes (e.g. 100-250 mL). Since the concentration in the product is linearly related to the exposure estimate in ART, assumption of a fourfold dilution would result in a modelled exposure estimate slightly below the monitoring-based value.

Due to the extensive coverage of the monitoring data and based on the discussion above, the long-term TWA based on the 90th percentile of the monitoring data (0.48 ng/m³) has been used in the former aggregated exposure assessment and risk characterisation (see section 9.1.6). The exposure estimate under consideration of the future situation at the SCB Bussi plant (0.096 ng/m³) will be used in this CSR for risk characterisation.

Final exposure estimate for task 3: 0.096 ng/m³

9.1.5. Worker contributing scenario 4: T4: Maintenance and cleaning (PROC 8a)

9.1.5.1. Conditions of use

Maintenance of pumps and cleaning with water hose; the following descriptions from ART primarily relate to maintenance (the activity modelled in ART)

	Method
Product (article) characteristics	
• Concentration of substance in mixture: = 0.184% <i>Concentration of Cr(VI) based on SD concentration of 6.5 g/L in the electrolyte and a density of the electrolyte of 1400 g/L. Maintenance (repair of pumps) assumed to represent contact with this solution.</i>	External Tool (ART 1.5)
• Product type: Powders dissolved in a liquid or incorporated in a liquid matrix	External Tool (ART 1.5)
• Viscosity: Liquids with low viscosity (like water)	External Tool (ART 1.5)
Amount used (or contained in articles), frequency and duration of use/exposure	
• Duration of activity: 60 minutes	External Tool (ART 1.5)
• Frequency of use/task: = 48 days per year (maintenance) <i>Weekly maintenance assumed as worst case, but will often be less frequent.</i> • Frequency of use/task: = 96 days per year (cleaning with water hose) <i>Twice per week for cleaning for 60 min/event (i.e. 120 min/week); alternatively, cleaning every day for up to 20 minutes is also covered.</i>	External Tool (ART 1.5)
Technical and organisational conditions and measures	

	Method
• Place of use: Indoors - 1000 m ³	External Tool (ART 1.5)
• Ventilation rate of general ventilation system: 10 ACH	External Tool (ART 1.5)
Conditions and measures related to personal protection, hygiene and health evaluation	
• Surface contamination/fugitive emission sources: The process is not fully enclosed and the integrity of that enclosure is not regularly monitored, but effective housekeeping practices are in place.	External Tool (ART 1.5)
• Chemical protection clothing or protective apron as well as rubber boots when cleaning with a water hose	
• Wear chemically resistant gloves (tested to EN374) in combination with specific activity training.	
• Respiratory Protection: Yes (Respirator with APF of 20) [Effectiveness Inhal: 95%] when aerosol formation occurs (e.g. during cleaning with a hose)	External Tool (ART 1.5)
Other conditions affecting workers exposure	
• Primary emission source proximity : The primary emission source is located in the breathing zone of the worker (near field, < 1 m)	External Tool (ART 1.5)
• Activity class and subclass: Handling of contaminated objects	External Tool (ART 1.5)
• Falling liquid (transfer rate): 0.1 - 1 L/min	External Tool (ART 1.5)
• Handling of contaminated objects (size of object): Activities with treated/contaminated objects (surface 0.1-0.3 m ²) <i>Covers areas on the object of 55 cm x 55 cm, believed to cover connecting ends of larger pumps.</i>	External Tool (ART 1.5)
• Handling of contaminated objects (degree of contamination): 10-90% of surface <i>High level of contamination assumed</i>	External Tool (ART 1.5)

9.1.5.2. Exposure and risks for workers

Air monitoring results

No monitoring results for maintenance tasks are available, since these are infrequent and cannot be planned for inclusion in the monitoring campaign. Since cleaning with a water hose (the cleaning activity considered to be associated with aerosol exposure) is also infrequent at many sites or was not performed for safety reasons (electrical supplies for monitoring pumps lying on the floor), only three monitoring results from one site are available. Monitoring was performed during the cleaning of electrolysis cells with a hose (see Figure A4-16 in Annex 4). However, it turned out that two additional monitoring points originally assigned to task 5 (waste handling) in fact reflect cleaning activities at and around filter presses (cleaning with a water hose, see Figure A4-17 in Annex 4). These were therefore also included in the evaluation for task 4 and the result is shown in the following table (full descriptive statistics for the entire set is included in Annex 3A).

Table 23. Monitored exposure for workers: task 4 (cleaning)

No. of sites covered	No. of measurements	Measurements <LoQ	Frequency (d/a)	Duration [min/shift]	Inhalation exposure [ng/m ³]	
					Monitoring result	Long-term TWA
1	3	0	96	60	136* (without RPE)	
1	3	0	96	60	6.8 (with RPE)**	0.34**

All calculated values (TWA, long-term) rounded to two significant figures for presentation, but unrounded values used for calculation of exposure; * Maximum of three values (21.8, 71.8 and 136 ng/m³, AM: 76.5 ng/m³); ** includes reduction by 95% due to respiratory protection (half mask with P3 filter or full mask with P3 filter or P3 combination filter).

Note that the worker performing this task during the monitoring campaign did not wear respiratory protection

(see Figure A4-17 in Annex 4). Interviews with workers performed at the sites indicate that some, but not all workers wear respiratory protection during cleaning with a water hose. On the basis of the results of the monitoring campaign respiratory protection is now prescribed for such activities.

Modelling results

The modelled exposure estimates are shown in the following table.

Table 24. Modelled exposure for workers: task 4 (maintenance)

Frequency (d/a)	Duration [min/shift]	Inhalation exposure [ng/m ³]		
		Task-based	TWA (on day of exposure)	Long-term TWA
48	60	7.5*	2.0	0.19

All calculated values (TWA, long-term) rounded to two significant figures for presentation, but unrounded values used for calculation of exposure; full ART reports are attached in Annex 5. * 75th percentile (see text for details)

The modelled exposure estimates are based on (also see section 9.0.2.3):

- the maximum SD concentration of 0.464% (0.184% Cr(VI))
- an exposure duration of 60 minutes
- a high frequency of weekly repair of a pump, which may appear over conservative

It is inherent in maintenance tasks (e.g. repair of pumps, valves etc.) that they are often unforeseeable and their frequency may be highly variable, i.e. months with 2-3 repairs and months without any repairs at all (at least in the context of relevant SD exposure). In addition, the duration of such tasks may be quite long, but the actual exposure duration may be much shorter, e.g. exposure during dismantling of equipment and cleaning activities, but not during the actual repair.

Therefore, the approach chosen uses the maximum SD concentration of the electrolyte solution (likely to be present in parts requiring repair, but most probably not at all sites) in combination with more realistic assumptions on exposure duration and frequency (also see section 9.0.2.3). This is believed to also cover exposures during less frequent activities, but uncertainty remains in relation to this estimate.

As another conservative element, exposure was modelled as near-field exposure within ART, assuming that the worker remains close to the emission source (i.e. breathing zone of the worker within 1 m of the emission source) for the entire exposure duration of 60 minutes. This can be considered very conservative for this type of task. If the same task with the same input parameters is modelled in ART as far-field exposure (i.e. breathing zone of the worker more than 1 m from the emission source), the task-based concentration is reduced from 16 to 0.7 ng/m³. Annex 5 also presents the ART report for this scenario.

Finally, the assumptions on the surface area (0.1-0.3 m²) and the degree of contamination (10-90% of the surface) were checked for their impact on the exposure estimate, since they may also be highly variable (see section 9.0.2.3 for the rationale for these assumptions). Additional modelling exercises within ART showed that the surface area has no additional impact, i.e. increasing it to the maximum value (> 3 m²) does not lead to an increase in the exposure estimate if the same degree of contamination is selected. This finding is due to the fact that ART models inhalation exposure from the handling of objects contaminated with powders dissolved in liquids (as in the present case) with an aerosol weighting factor that is independent of the surface area, but only dependent on the degree of contamination (Fransman et al., 2010). As a consequence, ART near-field estimates for the task addressed here range between 5.4 (< 10% contamination) and 54 ng/m³ (> 90% contamination), with the task-based value derived above (16 ng/m³) reflecting 10-90% contamination.

Overall, these considerations increase the confidence that the exposure estimates in fact represents a conservative exposure estimate for maintenance activities for this use.

In contrast to ART modelling estimates for other tasks, the 75th percentile (rather than the upper inter-quartile confidence interval of the 75th percentile that is similar to the 90th percentile, see section 9.0.2.3) was chosen for this activity. There are two reasons for this selection:

- Task 4 covers two different activities: cleaning with a water hose (see monitoring data above) and maintenance tasks (modelling results presented here). Since

- the maximum of the monitoring values was used for cleaning activities and
 - both estimates are added up to derive an exposure estimate for task 4
- application of the 75th percentile still represents a conservative approach.
- The exposure estimate for task 4 will be combined in the aggregated exposure estimate in section 9.1.6 with 90th percentiles (or similar values) for tasks 1 and task 2.

In order to prevent an over-conservative combination of upper end percentiles/maximum values in the aggregated estimate, the task 4 estimate is based on the maximum for cleaning and the 75th percentile for maintenance.

Based on the experience from the Caffaro Brescia site it is currently assumed, that assumptions for task 4 are applicable without further changes to the SCB Bussi site, i.e. cleaning activities will not exceed 120 minutes per week and maintenance will not be performed more than once per week. However, due to the fact that the SCB Bussi site will be newly constructed and follow the current state of the art a lower frequency for maintenance activities seems to be more realistic. Therefore, the estimate for the exposure during maintenance seems to be very conservative. Also the long-term TWA for cleaning resulting on basis of the monitoring values is probably very conservative for the SCB Bussi site as the total SD concentration in the brine is lower than assumed for the former Caffaro Brescia CSR (<5% vs. 6.5%). However, in the absence of more site specific experience the exposure estimates of the former Caffaro Brescia CSR are also used for the exposure assessment of the SCB Bussi site.

Discussion and conclusions

In summary, monitored and modelled long-term inhalation exposure to Cr(VI) was estimated to be:

- Monitoring (cleaning with a water hose): 0.34 ng/m³ (n=3, maximum used)
- ART modelling (maintenance): 0.19 ng/m³ (conservative estimate)

Note that both estimates relate to very different tasks and respiratory protection was applied to the estimate for cleaning activities, while it was not for the maintenance tasks. Therefore, the agreement in the estimates cannot be taken as supportive information of either estimate. Rather, the two different approaches suggest a similar exposure range during diverse maintenance and cleaning activities. The activity monitored (cleaning with a water hose) could not be modelled with ART, since no appropriate model exists.

The estimates for long-term inhalation exposure during cleaning were derived from monitoring data obtained by static sampling (necessary to obtain a sufficiently low LoQ, see section 9.0.2.3). Therefore, the monitoring data are somewhat uncertain in relation to actual exposure in the breathing zone of workers. In contrast to “classic” stationary sampling, however, which is typically designed to monitor exposure in the general work area, stationary sampling during the monitoring campaign was performed close to the potential sources of exposure for task 4 and the location of the worker during this task (i.e. close to the worker when cleaning with a hose).

There is some additional information from the monitoring campaign. At one site, removal of an electrolysis cell and cleaning of electrodes was performed in the cell room five days before the monitoring. Loading of the cleaned electrodes for shipment was performed during the first day of monitoring, with dust particles being visible on the floor below the cleaned electrodes (SD content could not be ascertained; reddish colour most probably due to iron). This loading operation took place within 2.5-5 m of one monitoring point (see Figure A4-18 in Annex 4). Cr(VI) concentrations at this monitoring point (and, in fact, the other monitoring point in the same cell room) were below the LoQ on both monitoring days (n=4). While these data only relate to the last activities in this maintenance tasks, they nonetheless demonstrate that the cleaning and maintenance activities performed before the monitoring did not lead to a contamination resulting in elevated Cr(VI) concentrations afterwards.

Since the cleaning and maintenance tasks covered here relate to two different tasks that are both infrequent, the two estimates will be added up as already discussed above. Overall, the long-term TWA of (0.34 ng/m³ + 0.19 ng/m³) 0.53 ng/m³ will be used in the aggregated exposure assessment and risk characterisation (see section

9.1.6).

Final exposure estimate for task 4: 0.53 ng/m³

9.1.6. Aggregated exposure estimation and risk characterisation for unit operators

9.1.6.1 Exposure estimation

Aggregation rationale

This section aggregates the exposure estimates of unit operators engaged in the four tasks described in section 9.1.2-9.1.8. For such an aggregation, addition of all long-term TWA would be the simplest option. However, one and the same worker does not perform all tasks with the indicated frequencies over the entire year. In particular, tasks that are not performed daily (T4) are carried out by other staff members than those involving the regular running of the unit with the daily tasks of sampling and production lab analysis (T2 and T3) that are indeed regularly performed by the same workers (i.e. unit operators, although these take turns during their shift, see below). This aggregation has been adapted to the future activities at the Bussi sul Tirino site of SCB.

Based on the current plans of SCB the following aggregation was chosen in order to represent the situations present in the Bussi sul Tirino site.

The following table reveals the number of workers engaged in sodium chlorate production of the applicant.

Table 25. Shift patterns for aggregated exposure estimation

Worker	Number of workers	Assumptions for aggregation
Unit operator	2 unit operator per shift per site 3 shifts per site per day 5.5 shift teams -> 11 unit operators per site	One unit operator performs one half of all sampling and production lab analyses (T2 + T3) per shift, the other half being carried out by the second unit operator. This is a conservative approach as the analysis during normal working time will be performed by the central lab operators. Unit operators also perform cleaning activities (T4).
Supervisor	1 supervisor per shift per site 3 shifts per site per day 6 shift teams -> 6 supervisors per site	Not engaged in specific tasks T1-T4
Mechanical day worker (internal)	4 mechanical day workers (workers who are not part of the shift system, there are at least two mechanical day workers per day	The worker can be involved in dismantling pumps and valves and the associated cleaning activities (task 4) and in the cleaning of the candle filter after cleaning of the filter (not regarded in exposure assessment as only small residues of Cr(VI) will remain after cleaning).
Lab	1 lab supervisor	Not engaged in T5

* Day workers are e.g. maintenance workers, electricians and multifunctional workers

Table 27. Task-specific and aggregated long-term TWA inhalation exposure estimates for unit operators and mechanical day workers

Task	N	N (sites)	N<LoQ	Long-term TWA Cr(VI) concentration [ng/m ³] former CB CSR	Comments	Best estimates for SCB on Long-term TWA Cr(VI) concentration [ng/m ³]**
T1	2	1	100%	0.25	Based on modelling	0.063
T2	31	8	58%	1.4	Based on 90 th percentile of monitoring	0.958
T3	18	8	78%	0.48	Based on 90 th percentile of monitoring	0.096
T4	3	1	0%	0.34 (cleaning); 0.19 (maintenance)	Based on maximum of monitoring (cleaning) and modelling (maintenance)	0.34 (cleaning); 0.19 (maintenance)
Aggregated estimates						
Unit operator				1.26	T1 + T2 + T3 + T4 (cleaning)	0.73
Mechanical day worker				0.27	T4 (maintenance + cleaning)	0.27

All calculated values (TWA, long-term) rounded to two or three significant figures for presentation, but unrounded values used for calculation of aggregated exposure; aggregated exposure given with three significant figures.

N: Number of measurements; N (sites): Number of sites covered by measurements; N<LoQ: Number of measurements below the limit of quantification

* Value for T1 based on ART modelling also taken for the monitoring-based aggregated exposure, since the lower monitoring values (both < LoQ) are insufficient.

** Values for SCB calculated under consideration of predicted future values for duration and frequency of the specific tasks.

The following issues have to be considered when interpreting the data:

- The 90th percentiles based on the monitoring data were used when a sufficient number of samples from all companies were available (T2 and T3). As outlined in sections 9.1.3 and 9.1.4 ART modelling results for these tasks were in good agreement with the monitoring data. This demonstrates that the monitoring strategy (stationary sampling to obtain a sufficiently low limit of quantification; monitoring pumps located close to sources of exposure rather than in general work areas) was adequate for the measurement of inhalation exposure of workers, since ART higher tier modelling reflects inhalation exposure in the breathing zone of workers.
- Maximum values of the monitoring campaign were used when the number of samples or the coverage of sites was less representative (T4 (cleaning)). In these cases, ART modelling could not be performed (T4 (cleaning)).
- Modelled values were chosen for the exposure estimate, when the monitoring-based value was lower but was of questionable representativeness (T1; n=1) or when no monitoring values were available (T4 (maintenance)).
- The monitoring data basis for T1, and T4 is more limited, since these are infrequent tasks and planning ahead for coverage by the monitoring campaign was impossible in most cases.
- Monitoring was performed over 8 hours during daytime and in most cases covered one half of two shifts each (since shifts often changed between noon and 2 pm). In addition, monitoring was performed on two consecutive days, with different workers sometimes covered on different days (depending on shift plans). The monitoring data therefore cover the variability between workers and between plants (also see discussion in sections 9.1.3 and 9.1.4 as well as the photo documentation in Annex 4). They are therefore considered reliable and representative of the use of SD covered by this CSR.
- The aggregated estimate is conservative since
 - input values for modelling and assumptions on duration and frequency (also applied to the monitoring results to calculate long-term TWAs) represent the maximum obtained across companies covered by this CSR,
 - the two aggregated estimates combine 90th percentiles or even maximum values (see **Table 27**) for 4 different tasks (T1, T2, T3 and T4 for unit operators). If the aggregated estimate is based on the 75th percentiles, the aggregated exposure was about two times lower for unit operators (0.61 instead of 1.2 ng/m³) in the former assessment.

Discussion

The long-term TWA Cr(VI) concentrations for unit operators and day workers were derived under consideration of a specific duration and frequency for the relevant tasks. This approach implies that exposure to Cr(VI) is negligible for a substantial part of the workday. Unit operators indeed spend most of the shift in the control room, where they visually control processes on control panels and video displays. Other tasks include visual checks of equipment and processes in the unit. However, these visual checks of equipment and processes are required in the actual cell rooms (where the samples are taken as well) that constitute a noisy environment. For this reasons alone, unit operators limit the time in the cell rooms during routine operations. Therefore, the assumption of negligible exposure during the rest of the shift appears justified. The monitoring results obtained during the generation of the former CSR further support this assumption. For example, even close to the sampling outlets more than half of the monitoring values (58%) are below the limit of quantification, with an even higher figure (78%) being below the limit of quantification in production labs. Even when comparatively high exposure levels were monitored at one monitoring point, Cr(VI) concentrations at the next nearest monitoring point in the same hall were not necessarily elevated. For example, two monitoring points within about 5-10 m of the monitoring point showing a relatively high Cr(VI) concentration (129.5 ng/m³; see Figure A4-10 in Annex 4) had consistently Cr(VI) concentrations below the limit of quantification on both monitoring days. These data strongly suggest that Cr(VI) exposure in other areas of the unit will be negligible.

Stationary sampling with high volume monitoring pumps was chosen for the monitoring campaign solely in order to achieve a sufficiently low limit of quantification that is impossible to achieve by personal sampling. Stationary sampling, however, may not fully cover actual breathing zone exposure of workers. In order to circumvent this drawback, the monitoring design involved the positioning of the monitoring pumps close to the sources of exposure rather than in general work areas. In some cases, this could not be fully achieved due to safety concerns (e.g. keeping fire exits clear etc.). However, the estimates based on ART modelling (aiming at inhalation exposure in the breathing zone of workers) strongly suggest that the monitoring design was adequate for the measurement of actual inhalation exposure of workers (see sections 9.1.2-9.1.5 for a comparison of monitoring and ART modelling results for the specific tasks).

The monitoring data indicate that inhalation exposure to Cr(VI) from the use of SD covered in this CSR is very low. This is due to several factors:

- General process design of a largely closed system
- Use of SD dissolved in a liquid (SD bought as a liquid solution and used in a liquid)
- Very low concentrations of SD in the process (corresponding to a maximum Cr(VI) concentration of 0.184%)

As a result, 61% of the monitoring values were below the limit of quantification. Even the maximum value measured during the monitoring campaign of about 768 ng/m³ (during a process no longer in use) was almost 4-times lower than the arithmetic mean of extensive measurements performed in various German industries (see section 9.1. for these data).

The aggregated exposures derived above are below the LoQ of the monitoring campaign (2.4 ng/m³), since a) the overall exposure was low for the reasons outlined above b) tasks associated with quantifiable exposure are not performed over the entire day, but only for a comparatively short duration of the shift and c) higher exposures were predominantly observed during infrequent tasks.

Overall, the following long-term TWA Cr(VI) concentrations are derived:

Final aggregated exposure estimates:

Unit operators	0.73 ng Cr(VI)/m³
Mechanical day workers	0.27 ng Cr(VI)/m³

9.1.6.2 Risk characterisation

The exposure estimate derived in section 9.1.6.1 was compared with the exposure-risk relationship (ERR) derived by ECHA (2013), according to which occupational exposure to 10 ng/m^3 is associated with an excess lung cancer risk of 4×10^{-5} (see section 9.0.3). The risk resulting from the application of this ERR to the inhalation exposure estimate presented above is shown in the table.

Table 28. Risk resulting from Cr(VI) exposure during its industrial use as a process chemical in sodium chlorite production

Workers	Task aggregation	Inhalation exposure [ng/m^3]	Risk
Unit operators	Task 1 + Task 2 + Task 3 + T4 (cleaning)*	0.73	0.29×10^{-5}
Mechanical day worker (internal)	Task 4 (maintenance + cleaning) **	0.27	0.11×10^{-5}

* One unit operator assumed to be performing one half of these tasks

** One mechanical day worker assumed to be performing one half of these tasks

Taking into consideration the inhalation DNEL systemic long-term for workers of $43 \text{ } \mu\text{g/m}^3$ with respect to effects on fertility the aggregated exposure estimates for unit operators (0.73 ng/m^3) and mechanical day workers (0.27 ng/m^3) would result in RCRs of 1.7×10^{-5} and 6.3×10^{-6} , respectively. These RCR values, which were only calculated for comparison, clearly document that carcinogenicity is the most relevant endpoint to be considered in risk assessment for inhalation exposure.

Conclusion on risk characterisation

The calculated risk for life-time exposure of operators to Cr(VI) under the described use conditions is below the value of 1×10^{-5} for unit operators and mechanical day workers. This is true for both calculations: the one performed during the former AfA for the consortium of sodium chlorate producing companies as well as for the one considering the site specific parameters of the future SCB Bussi plant.

It has to be emphasised that according to the information from the German Helpdesk all types of analytical work, including analytical work for quality control or for monitoring purposes and sampling for this purposes are considered scientific research and development. Therefore, they are exempted from authorisation according to Art. 56, No. 3 of REACH. I.e. these tasks formally need not to be considered in the exposure and risk assessment. But as these activities mainly contribute to the exposure of the unit operators they were considered in this risk estimate. Without consideration of these activities an about 3-fold lower risk would result for the unit operators.

The monitoring data from Caffaro Brescia as presented in Annex 3B reveal that the exposure at the Brescia site is even lower than the exposure calculated in this CSR for the future SCB site. Considering that the SCB site will be similar to the Brescia site but with relevant technical improvements it can be reasonably be assumed that the assessment presented here and which is mainly based on monitoring results at other sodium chlorate plants located in Europe should be regarded as a conservative worst case approach.

9.1.7. Worker contributing scenario 5: T5: Central lab analyses (PROC 15)

9.1.7.1. Conditions of use

Lab analyses of the electrolyte solution may involve analysis of the solution without dilution. Therefore, the initial concentration is retained (in contrast to analyses in the production lab)

	Method
Product (article) characteristics	

	Method
• Concentration of substance in mixture: = 0.184% <i>Concentration of Cr(VI) based on SD concentration of 6.5 g/L in the electrolyte and a density of the electrolyte of 1400 g/L.</i>	External Tool (ART 1.5)
• Product type: Powders dissolved in a liquid or incorporated in a liquid matrix	External Tool (ART 1.5)
• Viscosity: Liquids with low viscosity (like water)	External Tool (ART 1.5)
Amount used (or contained in articles), frequency and duration of use/exposure	
• Duration of activity: < 4 hours <i>Maximum duration for analyses in the central lab from survey of companies: 240 minutes/day</i>	External Tool (ART 1.5)
• Frequency of use/task: = 240 days per year	External Tool (ART 1.5)
Technical and organisational conditions and measures	
• Place of use: Indoors - any size workroom	External Tool (ART 1.5)
• Ventilation rate of general ventilation system: 3 ACH	External Tool (ART 1.5)
• Primary localised controls: Local exhaust ventilation: Enclosing hoods: Fume cupboard (99% efficiency)	External Tool (ART 1.5)
Conditions and measures related to personal protection, hygiene and health evaluation	
• Surface contamination/fugitive emission sources: The process is not fully enclosed and the integrity of that enclosure is not regularly monitored, but effective housekeeping practices are in place.	External Tool (ART 1.5)
• Wear chemically resistant gloves (tested to EN374) in combination with specific activity training.	
Other conditions affecting workers exposure	
• Primary emission source proximity: The primary emission source is located in the breathing zone of the worker (near field, < 1 m)	External Tool (ART 1.5)
• Activity class and subclass: Transfer of liquid products - falling liquid	External Tool (ART 1.5)
• Falling liquid (transfer rate): 0.1 - 1 L/min	External Tool (ART 1.5)
• Containment of the process: Handling that reduces contact between product and adjacent air	External Tool (ART 1.5)
• Transfer Loading Type : Splash loading, where the liquid dispenser remains at the top of the reservoir and the liquid splashes freely	External Tool (ART 1.5)

9.1.7.2. Exposure estimation

Air monitoring results

This task was not included in the monitoring campaign because a low exposure was expected due to the low concentration of SD in the samples and handling in the laboratory under a fume cupboard.

Modeling results

The modelled exposure estimates are shown in the following table.

Table 29. Modelled exposure for workers: task 5

Frequency (d/a)	Duration [min/shift]	Inhalation exposure [ng/m ³]		
		Task-based	TWA (on day of exposure)	Long-term TWA
240	240	0.84	0.42	0.42

All calculated values (TWA, long-term) rounded to two significant figures for presentation, but unrounded values used for

calculation of exposure; full ART reports are attached in Annex 5.

The modelled exposure estimates are based on (also see section 9.0.2.3):

- the maximum SD concentration of 0.464% (0.184% Cr(VI))
- a maximum exposure duration of 240 minutes (relevant for inhalation exposure only) based on survey data (range 6-240 minutes)
- a daily task frequency

As a consequence, the long-term inhalation estimate represents an upper end not existing in reality, because the company reporting the maximum concentration also reported a lower task duration for central lab analyses of 60 minutes.

It is currently assumed, that assumptions on frequency and duration for task 5 are more or less applicable to the future situation in the central lab of the SCB Bussi site. However, a daily exposure duration of 240 minutes seems to be a little bit conservative and will probably be shorter (only about on average 80 minutes per day), however, due to the inherent insecurity to this assumption the former exposure assessment is also transferred to the SCB Bussi situation. This is a conservative approach due to the fact that a) exposure during lab analysis has not to be regarded during an AfA, b) the SD concentration in the brine in SCB Bussi will be lower than in the former assessment for Caffaro Brescia, c) mostly diluted solutions will be handled in the central lab, and d) a maximum value for the duration has been taken into consideration.

Discussion and conclusions

In summary, monitored and modelled long-term inhalation exposure to Cr(VI) was estimated to be:

- ART modelling: 0.42 ng/m³ (worst case)

The modelled long-term TWA for the central lab (0.42 ng/m³) is in the same order of magnitude as the calculated value for the production lab taking into account the future SCB parameters without consideration of a local exhaust ventilation (0.96 ng/m³). This is primarily due to chance. In fact, a comparatively low long-term TWA results for task 3 if the local exhaust ventilation (10% effectiveness) is taken into consideration (0.096 ng/m³), which is even lower than the long-term TWA calculated for the lab. This is not astonishing as in a worst case approach for the central lab no dilution of the SD containing solution was assumed. The finding that more than 75% of all production lab monitoring results are below the LoQ of 2.4 ng/m³ and the maximum was 2.4 ng/m³ (see section 9.1.4) suggests that the input chosen for ART modelling of task 5 was indeed very conservative.

Final exposure estimate for task 5: 0.42 ng/m³

9.1.7.2 Risk characterisation

The exposure estimate derived in section 9.1.8.1 was compared with the exposure-risk relationship (ERR) derived by ECHA (2013), according to which occupational exposure to 2.5 ng/m³ is associated with an excess lung cancer risk of 1×10^{-5} . The risk resulting from the application of this ERR to the exposure estimate presented above is shown in the table.

Additionally, for the risk calculation it is taken into account that there are 5 central laboratory operators, i.e. every operator is on average only exposed to 1/5 of the calculated TWA.

Table 30. Risk resulting from Cr(VI) exposure during its industrial use as a process chemical in sodium chlorate or chlorite production: lab staff (task 5)

Inhalation exposure [ng/m ³]	Risk
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0.084*	3.36×10^{-7}
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* One lab operator assumed to perform one fifth of these tasks

Conclusion on risk characterisation

The calculated risk for life-time exposure of lab staff to Cr(VI) under the described use conditions is well below the value of 1×10^{-5} . It has to be considered that this is a very conservative approach, as laboratory analysis has not to be included in the exposure and risk estimate.

9.2 Dermal exposure

Dermal exposure may in principle occur through splashes during sampling (T2), lab analyses (T3 and 5) and – less frequent – during feeding SD (T1) and cleaning and maintenance (T4). Task 5 (waste handling) is not relevant for the situation at the SCB plant in Bussi sul Tirino as the filter press will be removed by a candle filter which does not require regular activities by the workers. In fact, the candle filter will probably only require maintenance once or twice a year (not more than 4 times per year). For further details see section See Table 5.

Modelling dermal exposure during the use of SD covered by this AfA is difficult. The substance is a solid dissolved in a liquid and is therefore outside the applicability domain of the standard modelling tool ECETOC TRA. The Riskofderm model (v.2.1) does not contain adequate modules (DEO units) for T1 (handling contaminated objects), and T4 (cleaning tasks such as cleaning with a water hose). Tasks covered by T2, T3 and T5 may be modelled as filling tasks (DEO unit 1 in Riskofderm). The conditions of use applied for the Riskofderm model are described in the following table.

9.2.1 Conditions of use (Riskofderm modelling, realistic input, for details see Annex 8)

	Method
Product (article) characteristics	
• Physical form of the used product: Liquid	Riskofderm 2.1
Amount used (or contained in articles), frequency and duration of use/exposure	
• Duration of dermal exposure: = 30 min	Riskofderm 2.1
• Frequency of skin contact: Rare contact	Riskofderm 2.1
• Use rate of the product - liquids: ≤ 0.5 L/min	Riskofderm 2.1
Technical and organisational conditions and measures	
• Level of automation of the task: Manual task	Riskofderm 2.1
Conditions and measures related to personal protection, hygiene and health evaluation	
• Dermal protection: Yes (Chemically resistant gloves conforming to EN374 with specific activity training) and (other) appropriate dermal protection [Effectiveness Dermal: 95%]	Riskofderm 2.1
Other conditions affecting workers exposure	
• Generation of aerosols or splashes during task: No	Riskofderm 2.1

	Method
• Type of skin contact: Light skin contact	Riskofderm 2.1

A second modelling approach using a default dermal load of 0.1 mg/cm²/d (EU RAR for SD for non-dispersive uses) was also followed. This approach allowed estimating dermal exposure during all tasks, including any body exposure during cleaning with a water hose and provides estimates of possible dermal exposure.

Modelling results

The modelled exposure estimates for T2, T3 and T6 are shown in the following table. In Annex 8 details are also given for the unrealistic exposure scenario described above. In Table 32 the actual dermal exposure to Cr(VI) based on input data from the EU RAR (generic approach) are shown.

Table 31. Modelled Exposure for Workers: T2 (hands), T3 (hands), and T5 (hands) based on Riskofderm

Parameter	Unit	T2 (hands)	T3 (hands)	T5 (hands)	Rationale (Reference)
Potential dermal exposure to product per event	mg	137	137	137	Riskofderm result
Body weight	kg	70	70	70	Body weight for workers (Guidance IR & CSA, R.8 (ECHA, 2012a))
Potential dermal exposure to product	mg/kg bw/d	1.96	1.96	1.96	Calculated
PPE efficiency (gloves, protective clothing or apron)	%	95	95	95	See CSR
Actual dermal exposure to product	mg/kg bw/d	0.098	0.098	0.098	Calculated
Cr(VI) concentration in product	%	0.184	0.092	0.184	See Table 6 in the CSR
Actual dermal exposure to Cr(VI)	µg/kg bw/d	0.180	0.0900	0.180	Calculated

All values rounded to three significant figures, but unrounded values used in calculation

Using realistic inputs, dermal exposure to Cr(VI) is estimated to 0.180 µg/kg bw/d. Several input parameters involve a subjective element (e.g. in the judgement, whether contact is rare or light). Therefore, these input values were set to worst case values (more than rare contact, more than light contact, significant amounts of aerosols or splashes), although these do not represent the situation in reality and are unrealistic, all the more if combined. Using these unrealistic input parameters, the exposure (in mg product) is estimated to 4180 mg, corresponding to an actual Cr(VI) exposure of 5.49 µg/kg bw/d (all input values and calculations for the realistic and the unrealistic input are shown in Appendix 8).

Table 32. Modelled Exposure for Workers for all tasks based on a default dermal load of 0.1 mg/cm²/d (generic approach)

Parameter	Unit	T1 (hands)	T2 (hands)	T3 (hands)	T4 (hands)	T4 (body)	T5 (hands)	Rationale (Reference)
EU RAR modelling assumption (0-0.1 mg/cm ² /d)	mg/cm ² /d	0.1	0.1	0.1	0.1	0.1	0.1	Upper end of range (EU RAR (ECB, 2005)) from EASE for non-dispersive use with direct handling with incidental contact - > similar to the ones relevant here
Skin contact area	cm ²	480	480	480	480	8750	480	One side of both hands used as a conservative assumption; for T4 (body) one half of the body surface is assumed as a worst case, contact area from ECETOC

								TRA consumer module (ECETOC, 2009; 2012)
Dermal load	mg/d	48	48	48	48	875	48	Calculated
Body weight	kg	70	70	70	70	70	70	Body weight for workers (Guidance IR & CSA, R.8 (ECHA, 2012))
Potential dermal exposure to product	mg/kg bw/d	0.69	0.69	0.69	0.69	12.50	0.69	Calculated; identical to PROC 3 estimate (Batch manufacture of a chemical or formulation where the predominant handling is in a contained manner, e.g. through enclosed transfers, <u>but where some opportunity for contact with chemicals occurs, e.g. through sampling</u>); one hand face only assumed in ECETOC TRA
PPE efficiency (gloves, protective clothing or apron)	%	95	95	95	95	80	95	For hand exposure, see CSR; for T4 (body) a lower efficiency of 80% is assumed (HEEG Opinion 9)
Actual dermal exposure to product	mg/kg bw/d	0.0343	0.0343	0.0343	0.0343	2.500	0.0343	Calculated
Cr(VI) concentration in product	%	28	0.184	0.092	0.184	0.184	0.184	See Table on critical input parameters in the CSR
Actual dermal exposure to Cr(VI)	µg/kg bw/d	9.60	0.0631	0.0315	0.0631	4.60	0.0631	Calculated

With this generic approach the highest actual dermal Cr(VI) exposures were calculated for T1 (9.60 µg/kg bw/d) and body exposure in T4 (4.60 µg/kg bw/d). In both cases, these values are uncorrected for the lower frequency of these tasks, especially in T1.

Discussion and conclusions

In summary, modelled long-term dermal exposure to Cr(VI) was estimated to be:

- Riskofderm modelling: T2: 0.180 µg/kg bw/d
T3: 0.0900 µg/kg bw/d
T5: 0.180 µg/kg bw/d
- Generic modelling: T1 (hands): 9.60 µg/kg bw/d
T2 (hands): 0.0631 µg/kg bw/d
T3 (hands): 0.0315 µg/kg bw/d
T4 (hands): 0.0631 µg/kg bw/d
T4 (body): 4.60 µg/kg bw/d
T5 (hands): 0.0631 µg/kg bw/d

9.2.2 Exposure and risks for workers (dermal exposure)

The exposure concentrations and risk characterisation ratios (RCR) for dermal exposure are reported in the

following table.

Table 33. Exposure concentrations and risks for workers (dermal exposure)

Task	Exposure concentration	Risk quantification
T1 (generic modelling)	9.60 µg/kg bw/d	RCR = 0.223
T2 (Riskofderm)	0.180 µg/kg bw/d	RCR = 0.00419
T2 (generic modelling)	0.0631 µg/kg bw/d	RCR = 0.00147
T3 (Riskofderm)	0.0900 µg/kg bw/d	RCR = 0.00210
T3 (generic modelling)	0.0315 µg/kg bw/d	RCR = 0.000733
T4 (generic modelling, hands)	0.0631 µg/kg bw/d	RCR = 0.00147
T4 (generic modelling, body)	4.60 µg/kg bw/d	RCR = 0.107
T5 (Riskofderm)	0.180 µg/kg bw/d	RCR = 0.00419
T5 (generic modelling)	0.0631 µg/kg bw/d	RCR = 0.00147

Conclusion on risk characterisation:

In summary, compared with the dermal DNEL for workers of 43 µg/kg bw/d resulting RCRs are way below 1 for all tasks and the two modelling options and the risk is therefore adequately controlled.

Combined dermal exposure

For Unit operators and Day workers tasks that are performed over a working shift have to be combined and the aggregated RCR for dermal exposure can be calculated. The results are shown in the following table. For calculation of dermal exposure the individual exposure estimated calculated above are summed up and the RCR based on this combined exposure is calculated.

In a conservative approach, the higher exposure concentration was selected for tasks in case that the estimates were calculated with two different approaches (T2, T3, T5, calculated with Riskofderm and generic approach). For T4 the estimates calculated for body exposure and hand exposure were combined, since whole body exposure and exposure of hands is possible during cleaning and maintenance processes.

Table 34. Combined RCRs resulting from Cr(VI) exposure during its industrial use as a process chemical in sodium chlorite production

Workers	Task aggregation	Dermal exposure [µg/kg bw/d]	RCR
Unit operators	Task 1 + Task 2 + Task 3 + Task 4	14.53	0.34
Day workers	Task 4	4.66	0.11

In summary, compared with the dermal DNEL for workers of 43 µg/kg bw/d combined RCRs for dermal exposure of Unit operators and Day workers are below 1 and the risk is therefore adequately controlled.

10. RISK CHARACTERISATION RELATED TO COMBINED EXPOSURE

10.0 Human health – Qualitative Risk Characterisation of acute dermal and inhalation toxic effects and local effects on skin, eyes and respiratory tract at the workplace

Identification of hazard phrases

- Acute dermal toxicity Cat 4 (H312)
- Acute inhalation toxicity Cat 2 (H330)
- Skin corrosion Cat 1B (H314)
- Respiratory sensitisation Cat 1 (H334)
- Skin sensitisation Cat 1 (H317)

According to Table E.3-1 in ECHA Guidance on IR and CSA; Part E, this leads to

- high hazard band based on
 - o Acute inhalation toxicity Cat 2 (H330)
 - o Respiratory sensitisation Cat 1 (H334)
 - o Skin sensitisation Cat 1 (H317)
- medium hazard band based on
 - o Skin corrosion Cat 1B (H314)

No specific considerations are needed for acute dermal toxicity category 4.

Exposure routes

This qualitative risk characterisation is relevant for all occupational scenarios. Principally relevant exposure routes are inhalation and dermal exposure and the potential for occurrence of local effects after such exposure. The substance is of low volatility. Dermal exposure via the vapour phase is highly unlikely. Long-term inhalation exposure has been considered in the previous sections in a quantitative way. Therefore, this assessment focusses on local effects to skin and eyes after direct contact as well as short-term inhalation exposure.

Concentrations in mixtures

The maximum concentration of the submission substance handled in this use is a 70% aqueous solution. After addition of this concentrated solution to the production process a rapid dilution to an average concentration of up to 6.5 g/L (about 0.464% taking into consideration the density of the electrolyte) takes place. This reduces the risk for severe burns compared to handling the pure substance or concentrated solution. This is also below the general limits for classification for corrosive properties (1%), but not below the limit for classification of sensitising properties 0.2%. But this risk reduction is not taken into account when establishing the exposure scenarios, to ascertain maximum protection towards this substance of very high concern.

Exposure assessment

An exposure assessment has been performed and an exposure scenario for this use was established. The substance is mainly handled in closed systems, but several activities were identified, which include the possibility for direct contact. Contact intensity and duration is minimised for many of these activities (e.g. exposure is restricted to activities such as coupling/uncoupling of filling lines; sampling to be performed as submerged loading).

Nevertheless, there remain activities for which direct contact cannot be excluded. ECHA Guidance on IR and CSA, Part E, identified relevant conditions of use and risk management measures to control risks for local

effects from these activities.

Qualitative risk characterisation

Table E.3-1 recommends the following general operational conditions and RMMs for skin and respiratory sensitiser substances in the high hazard band:

- Any measure to eliminate exposure should be considered;
- Very high level of containment required, except for short term exposures e.g. taking samples;
- Design closed system to allow for easy maintenance;
- If possible keep equipment under negative pressure;
- Control staff entry to work area;
- Ensure all equipment well maintained;
- Permit to work for maintenance work;
- Regular cleaning of equipment and work area;
- Management/supervision in place to check that the RMMs in place are being used correctly and OCs followed;
- Training for staff on good practice;
- Procedures and training for emergency decontamination and disposal;
- Good standard of personal hygiene
- Recording of any 'near miss' situations
- Sensitizers – Without prejudice to relevant national legislation, pre-employment screening and appropriate health surveillance

In addition, the following personal protection equipment is recommended for Carc. Cat. 1 substances

- Substance/task appropriate respirator;
- Substance/task appropriate gloves;
- Full skin coverage with appropriate barrier material;
- Chemical goggles.

By duly applying risk management measures derived by the registrant of SD and communicated via the SDS the risk for these local effects is reduced as much as possible so that under normal operational conditions no risk to acute dermal and inhalation toxic effects and local effects on skin, eyes and respiratory tract have to be suspected. That risk management measures are applied properly is underlined by the fact that in none of the production sites of these companies any case of skin sensitisation due to use of chromium (VI) at the workplace was ever identified.

10.1. Human health

10.1.1. Workers

Combined exposure of workers involved in different tasks at the site is covered by the aggregated exposure assessment and risk characterisation presented above in sections 9.1.6 (inhalation exposure) and 9.2 (dermal exposure).

10.1.2. Consumer

Exposure assessment and risk characterisation is not applicable as there are no consumer-related uses for the substance addressed in this CSR.

10.2. Environment (combined for all emission sources)

As sodium dichromate is not listed in REACH Annex XIV due to environmental effects, no environmental exposure assessment is performed here.

Man via environment

Exposure of humans via the environment and associated risks are discussed and presented in Section 9.1.1. above (local and regional scale).

10.2.1. All uses (regional scale)

Not relevant as no environmental assessment is performed.

10.2.2. Local exposure due to all wide dispersive uses

Not relevant as no environmental assessment is performed and there are no wide dispersive uses covered in this CSR.

10.2.3. Local exposure due to combined uses at a site

Not relevant as no environmental assessment is performed and there is only one use covered in this CSR.

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