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Strategy for sediment quality assessment in Switzerland

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Summary

Introduction: This report presents a strategy for monitoring and assessing the quality of sediments based on their chemical status. This is a robust approach designed for routine checks. The method proposes a procedure for the collection and pre-treatment of samples for chemical analysis. It also proposes sediment quality criteria (SQC) for a list of relevant contaminants as well as a sediment quality classification system in accordance with the modular stepwise procedure.

Study design and sampling strategy: The method recommends collecting replicates from each site at three different points a few meters apart and combining them into a composite sample which will then be analyzed. For most study purposes and types of water bodies, the fraction <2 mm is proposed as a matrix for analysis. If, however, the monitoring aims at an analysis of trends and if the proportion of fine sediments is low, the recommended matrix is the fine fraction (<63 µm).

Substances proposed for sediment monitoring: A list of twenty substances is proposed for which it is recommended to collect information on environmental concentrations in sediment and to conduct a national risk assessment. This list includes four metals, four pesticides, two pharmaceuticals, a bactericide, a fluorinated surfactant, a phthalate, nonylphenols and octylphenols, a synthetic musk, a chlorinated aliphatic compound, and the groups of PCBs, PAHs and PBDEs. This list should not be used in all cases but can be adapted according to the type of watercourse studied, the sources of contamination present and the objectives of the study.

Sediment quality assessment: A two-level assessment method is proposed. Tier 1 consists of the chemical analysis of the substances of interest and their comparison with the corresponding sediment quality criteria (SQC). The SQC are derived from ecotoxicological data and correspond to threshold concentrations above which a risk of adverse effects for benthic organisms cannot be excluded. Depending on the relationship between the measured environmental concentration and the SQC, the sediment quality can be divided into five quality classes.

The evaluation system proposed to assess the quality of the sediment is based on five classes defined according to the value of the risk quotient (RQ). It is recommended to use the SQC as references or screening tools. Concentrations below the SQC indicate substances and sites of low ecotoxicological concern. The potential risk highlighted by exceeding the SQC at the first level of investigation (Tier 1) requires confirmation by a more detailed and site-specific assessment at Tier 2. Available tools to refine the exposure and / or effect assessment are briefly described.

Conclusions and perspectives: This approach is a first step towards harmonizing the evaluation of sediment quality in Switzerland. It is based on practices already widespread at the national level in order to ensure a certain continuity of the existing databases. The list of substances proposed for the monitoring of sediments is mainly based on previous prioritization exercises and the properties of the compounds given that data on measured environmental concentrations are still scarce for Swiss sediments. Therefore, the list must be regularly updated according to new

data from measurement campaigns or regulatory actions pertaining to chemical substances. Likewise, the SQC should be updated as scientific knowledge improves. Future improvements to the method will concern, in particular, toxicity due to mixtures of compounds and the development of a more detailed protocol for refining risk assessment.

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1. Introduction

1.1 Context

Sediments act as habitats and spawning sites for many aquatic organisms and represent therefore a key compartment of aquatic ecosystems, delivering important ecological functions and services (Wall 2004). However, they often act as a sink for various contaminants, which can pose a threat to aquatic organisms and negatively influence the critical functions sediments perform. Despite their importance, aquatic sediments have received little attention, particularly with respect to micropollutants such as pesticides or pharmaceutical products.

Contaminants enter aquatic systems through various pathways. The main sources of diffuse pollution to aquatic ecosystems are agriculture, urban areas and infrastructures (roads, railways), and to a minor extent waste deposits, aquatic activities and atmospheric deposition (Wittmer et al. 2014). Little research has been conducted on the extent of sediment contamination by diffuse inputs. However, a recent study in small streams from areas with intensive agriculture showed contamination of sediments by pesticides (Casado-Martinez et al. 2019). Several studies have also showed that point sources such as wastewater treatment plants and combined sewage overflows have negative impacts on sediment quality in Switzerland (Benejam 2016, Loizeau et al. 2017). In addition, sediments can also contain plastic wastes, which can also be contaminated with chemical compounds and may trigger ecotoxicological effects (Faure et al. 2015, Li et al. 2018). In the case of persistent organic pollutants, the contamination remains even after decades of substance release. Examples of persistent contaminants are PCBs and mercury, which are often associated with waste deposits and atmospheric depositions (Schmid et al. 2010, Ritscher 2018).

Contaminants will occur in a dissolved state in the water column or sorbed to sediment particles depending on their physico-chemical properties and the environmental conditions (Figure 1). The binding of chemical pollutants with sediment is a complex process, resulting from both absorption (physical entrapment) and adsorption (association on the surface of the different constituents from the sediment matrix). According to their properties (e.g. large specific surface areas, high ion exchange capacities), the fine and medium-sized particles (< 63 µm) are the most important scavengers of contaminants (Salomons and Brils 2004). Degradation mechanisms can also take place, decreasing the concentration of the parent compounds and leading to the presence of transformation products.

Aquatic organisms may be exposed to sediment-bound chemicals or their transformation products through direct contact or through ingestion of sediments and/or contaminated prey items (bioaccumulation and biomagnification), potentially leading to secondary poisoning higher in the food chain (Figure 1). Many processes are thus occurring at the same time, rendering the fate and effects of chemicals in the sediment compartment difficult to assess.

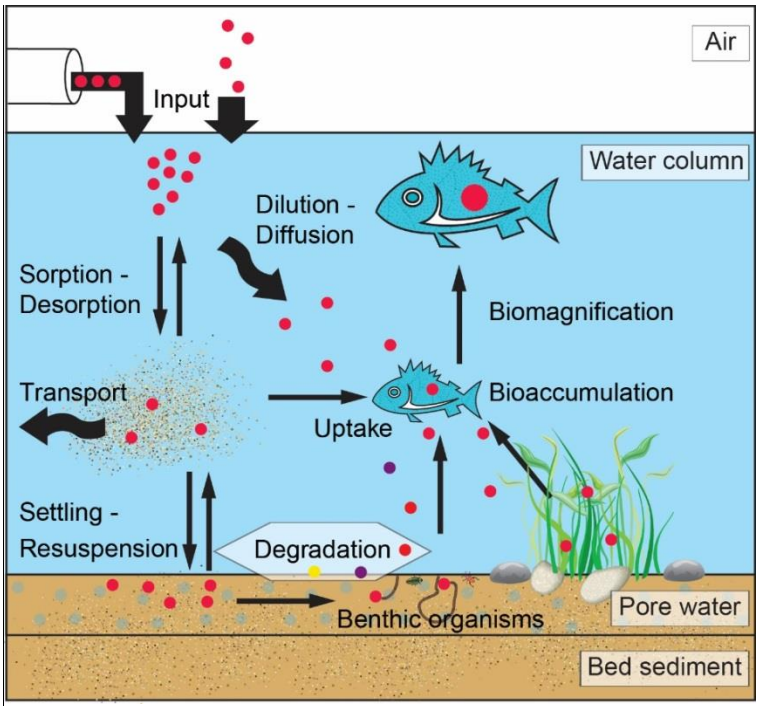

Figure 1: Conceptual model of sediment and trophic chain contamination dynamics.

1.2 Objectives and scope of application

This report presents a concept for sediment quality assessment and monitoring in Switzerland based on the chemical status of the sediment. It is a first step towards the harmonization of practices implemented among cantons in this area. It is not an enforcement aid of the FOEN but a guideline, which is designed to help Swiss cantonal authorities and other users screening and prioritizing sites and substances as well as identifying trends of sediment contamination. For other specific objectives such as contaminated sediment remediation, the concept presented here can be used as a starting point to trigger further investigations. For such purposes, this report incorporates recommendations to facilitate a more detailed risk assessment of the sediment compartment in the water body.

The method proposes a procedure for the collection and pre-treatment of samples for chemical analysis. It also proposes sediment quality criteria (SQC) for a list of relevant contaminants as well as a sediment quality classification system in accordance with the modular stepwise procedure (MSP). It is recommended to use the SQC as references or screening tools. The potential risk highlighted by exceeding the SQC at the first level of investigation (Level 1) requires confirmation by a more detailed and site-specific assessment.

This report was compiled in collaboration with experts from cantonal authorities, research institutes and the private sector. It is addressed to the authorities in charge of implementing environmental monitoring and to other professional partners active in this domain.

1.3 Organization of the report

This report is organized as follows:

- **Chapter 2**: provides the **legal framework in Switzerland** and other international frameworks and agreements.
- **Chapter 3**: provides a **situation analysis** of sediment quality assessment in Switzerland.
- **Chapter 4**: provides recommendations for the selection of substances for sediment monitoring and the list of **substances proposed for sediment monitoring in Switzerland** according to the present situation.
- **Chapter 5**: presents the recommendations for the **study design** (definition of study objectives, preparation of the **sampling strategy**, etc.). It also provides an overview of available analytical methods for the list of substances proposed for sediment monitoring.
- **Chapter 6**: includes recommendations for **sediment quality assessment** (methodology for the assessment of results from field campaigns with a classification system for sediment quality and a tiered approach for a more detailed sediment risk assessment using a two-tier approach).
- **Chapter 7:** provides conclusions and perspectives.

2. Legal framework

2.1. Legal framework in Switzerland

Water Protection Act and ordinance

The aim of the Water Protection Act of 24 January 1991 (WPA[1], SR 814.20) is to protect waters against harmful effects (WPA, SR 814.20, art. 1). Surface waters comprise the water bodies and their beds, including the bottoms and banks (art. 4a, WPA). It is prohibited to introduce, directly or indirectly, substances into a body of water liable to pollute it or to allow such substances to infiltrate (art. 6 para. 1, WPA).

The Water Protection Ordinance of 28 October 1998 (WPO[2], SR 814.201) defines ecological targets for surface waters (Annex 1, point 1, para. 3, letter b and c). According to these, water quality shall be such that suspended matter and sediments contain no artificial, persistent synthetic substances and that other potential water pollutants which can enter the water as a result of human activity do not accumulate in plants, animals, microorganisms, suspended matter or sediments.

In addition, substances that enter waters as a result of human activity must not adversely affect the reproduction, development and health of susceptible plants, animals and microorganisms (Annex 2, para. 11, al. 2 letter f, WPO).

Based on Art. 6 al. 1 (WPA), the authorities **can require emitters of substances to take measures** to prevent substances that accumulate in sediment from entering water, especially if these substances may pollute water or affect aquatic organisms[3].

If the water quality requirements in accordance with Annex 2 of the WPO are not met because the sediments are polluted, **remediation measures** must be taken in accordance with Art. 47 of the WPO. The same applies if, due to sediments, a particular use of the watercourse is no longer guaranteed (for example, use for drinking water, fishing, recreation, a nature conservation area, etc.). Remedial measures may also be necessary if sediment pollution causes damage to animals, for example through the consumption of fish in which substances from the sediment accumulate (Annex 2, para. 11 al. 2 letter f WPO). However, the mere fact that the sediment quality criteria developed within the framework of this project are exceeded is not sufficient to justify remediation measures within the meaning of art. 47 of the WPO.

The Modular Stepwise Procedure and the relevance of this strategy

Within the framework of the Modular Stepwise Procedure, standardized methods for the investigation and assessment of the status of rivers are being developed for Switzerland. The methods are used to record structural and hydrological, biological, chemical and ecotoxicological aspects of water quality in different stages with different processing intensities (Liechti et al. 1998). The

[1] Swiss Water Protection Act (WPA) (in French, LEaux).
[2] Swiss Water Protection Ordinance (WPO) (in French, OEaux)
[3] See the decision of the Federal Tribunal 1C_43 / 2007 of April 9, 2008, E. 2.4.

assessment is done by means of five different quality categories (http://www.modul-stufen-konzept.ch). The concept developed in this project falls within the framework of the MSP and aims to harmonize and improve the practices of cantonal authorities in terms of monitoring sediment quality. Although the developed quality criteria (SQC) are not numerical requirements in accordance with Annex 2 of the WPO, they do represent values that reflect current scientific knowledge on the effects of chemicals on aquatic organisms.

Further legal provisions and directives

- The **Contaminated Sites Ordinance** (CSO[4], SR 814.680, 1998) defines, among other things, when a site is considered to be a contaminated site. In addition to the soil and air, the surface water and groundwater are treated as protected environments and concentration limits for chemicals in the water or eluate of the contaminated site are given in Annex 1, which must not be exceeded. The enforcement aid "Polluted Sites and Surface Waters" deals with all questions pertaining to contaminates sites and surface water (FOEN, 2020).
- The **Ordinance of the Pollution of Soil** (OSol[5], SR 814.12, 1998) provides in Annexes 1 and 2 indicative, test and remediation limits for inorganic or organic substances in soils. These criteria are largely based on human toxicology data and are not specifically derived for sediments.
- The **Waste Avoidance and Waste Ordinance** (OLED[6], SR 814.600, 2015) defines thresholds for excavated material in Annex 3. If concentration limits provided are not exceeded, the material may be used to replenish material supply points or carry out approved terrain modifications. The excavated material also includes sediments used or produced in hydraulic engineering - for example, in the upgrading of rivers, the dredging of retention basins or the emptying of flood protection structures. Accordingly, this excavated material or sediment has to be reused according to the principles of Art. 19 OLED.
- The **enforcement aid Uncontaminated Excavation and Excavation Material in lakes within the framework of the Water Protection Act** addresses the question of when excavated material may be deposited in a lake and what factors must be taken into account (Wüest et al. 1999).
- The **Storm Wastewater Management Directive** from VSA[7] (2019) indicates how to assess water pollution from combined and storm water discharges. The pollutant load in sediments is also evaluated through calculation. Based on the results obtained, sediment analysis can be performed, as proposed in this report, to validate the results and develop suitable measures in the sewer network.

[4] Contaminated Sites Ordinance (in French, OCS).
[5] Ordinance of the Pollution of Soil (in French, OSol).
[6] Waste Avoidance and Waste Ordinance (in Frech, OLED).
[7] Swiss water association.

2.2. International laws and agreements

The European Union's Water Framework Directive

At European level, the Water Framework Directive (WFD), which aims at achieving "good ecological status of rivers" recommends not overlooking or ignoring sediment contamination, even if it is complex, because the ecological status of water bodies depends on it (EC 2000). Within the WFD, chemical monitoring is performed on sediments and biota mostly with the objective of assessing the long-term impacts of anthropogenic activities and ensuring that the existing levels of contamination do not increase to a stage that poses a threat to the environment and human health (EC 2010). Sediments are preferred for trend monitoring because the changes are not as fast as in the water column, thus reliable long-term comparisons can be carried out. While bottom sediments are the recommended matrix for monitoring some metals and hydrophobic compounds in marine and lentic water bodies (Maggi et al. 2012), suspended particulate matter are still preferred in lotic and dynamic water bodies (EC 2010). In addition, it is also recognized that sediment monitoring can also play a role when assessing impacts on environmental quality and in any investigative monitoring of pollutants' fate and behavior.

To prevent and reduce water pollution, the WFD requires that measured environmental concentrations be compared to Environmental Quality Standards (EQS). EQS are defined as "the concentration of a pollutant or group of pollutants in water, sediment or biota which should not be exceeded in order to protect human health and the environment" (EC 2010). These standards are developed for priority substances in accordance with a common implementation strategy for EU countries (EC 2011). The methodology for EQS derivation varies according to the protection objective (human health, biota, benthic invertebrates, pelagic organisms; EC 2011).

The monitoring of sediment and/or biota, with the water matrix, completes the picture of the status of water bodies. The legal framework states that "*Member States should have the possibility to establish EQS (for the existing 33 priority substances + 8 certain other pollutants) for sediment and/or biota at national level and apply those EQS instead of the EQS for water set out in the Directive*" (EC 2008), provided that these sediment/biota EQS ensure a level of protection equivalent to the EQS for water established at Community level. If Member States opt for applying EQS for these alternative matrices, monitoring shall take place at least once every year for mercury, hexachlorobenzene and hexachlorobutadiene, and for the other priority substances with a frequency of monitoring so as to provide sufficient data for a reliable long-term trend analysis (EC 2008, Art. 3).

A Technical Guidance Document (TGD No 25) was published in 2010 dedicated to harmonizing implementation strategies for sediment and biota chemical monitoring (EC 2010). This document includes recommendations for matrix selection for the monitoring of chemical pollutants in water bodies, general requirements such as statistical, data analysis, and quality assurance/quality control considerations, and recommendations for establishing appropriate monitoring programs (e.g. selection of sampling stations, sample replication, frequency). It also includes recommendations

for the application of other lines of information in addition to chemical measurements such as *in situ* communities, bioassays and/or bioavailability when EQS are exceeded yet entail a high level of uncertainty. This approach is largely in line with the recommendations existing in North America and elsewhere for sediment quality assessment (Wenning et al. 2005) and is in line with the recommendations in this document.

In practice, several European countries have established recommendations for sediment quality assessment, but EQS for the sediment matrix are scarce compared to EQS for surface waters and biota. Some countries have agreed to coordinate programs for the chemical monitoring of transboundary water bodies mainly within the framework of international commissions, such as the case of the Rhine (ICPR 2015).

The International Commission for the Protection of the Rhine (ICPR) Sediment Management Plan

The Convention on the Protection of the Rhine is the basis for international cooperation for the protection of the Rhine within the International Commission for the Protection of the Rhine (ICPR).

The ICPR set up a Sediment Management Plan (ICPR 2009) in recognition of the importance of sediment quantity and quality for the Rhine watershed. The main objectives of the ICPR Sediment Management Plan are to achieve balanced sediment processes and sustainable good sediment quality in order to achieve objectives of water and soil protection and to enable the disposal of dredged material without causing harm.

The implementation of the ICPR Sediment Management Plan includes an inventory with information on relevant amounts and sediment contaminations in the Rhine watershed as well as an assessment and classification of sediments to identify hots spots (or areas of highest risk for achieving good water quality). The ICPR Sediment Management Plan also includes proposals for measures and priorities for risk-oriented management of sediments and dredged material and for effective monitoring strategies for contaminated sediments as well as their potential remobilization. The ICPR Sediment Management Plan is supported by specific elements of the chemical component of the Rhine monitoring program, which includes the analysis of certain substances in suspended matter and the fluxes (ICPR 2015). It also includes a comparison with the evaluation criteria, the monitoring of sudden pollution, the collection of a data base for evaluating new problems, and a prioritization of emerging contaminants for setting monitoring and analysis strategies.

The measures to improve sediment quality identified by the ICPR Sediment Management Plan have been implemented in many locations but are in part still pending (ICPR 2020). The Program “Rhine 2040” requires the implementation of the measures identified in the ICPR Sediment Management Plan by 2025, transparent communication in the event of implementation problems and an examination of the updating of the Sediment Management Plan in close coordination with the planned work for the improvement of the sediment balance in the Rhine (ICPR 2020).

For the 2015-2020 objectives, the ICPR prefers suspended particulate matter to water samples for monitoring certain (organic) non-polar pollutants when levels of concentrations in the water

phase are below quantification limits, when water quality criteria are too low, or for the monitoring of trends and fluxes of non-polar and/or bioaccumulative substances[8]. Suspended particulate matter is also preferred over sediments in the 2015-2020 program in order to continue using the reference objectives included in the 2009 ICPR-SMP (ICPR 2009). However, the regulatory requirements from the WFD apply for the Rhine. Therefore, concentrations measured in suspended particulate matter are converted to total concentrations in water according to the quantity of suspended matter on the day of the sampling.

[8] For example, PAHs, PCBs, DEHP, tributyltin and its compounds, or the isomers of hexachlorocyclohexane.

3. Situation analysis of sediment quality in Switzerland

This chapter presents an overview of the situation of sediment quality monitoring in Switzerland as well as the state of sediment quality. The overview is based on several studies from the years 2012 to 2015. The full situation analysis can be found in the corresponding reports (Wildi et al. 2018 and Casado-Martinez et al. 2016).

3.1. Implementation of sediment quality assessments in Switzerland

According to information obtained in 2015, 14 of 26 cantons perform sediment sampling and analysis for chemical quality assessment on a more or less regular basis (Wildi et al. 2018). Among these, seven cantons have studied running waters (rivers/streams) while the other seven have assessed both running waters and lakes (Figure 2).

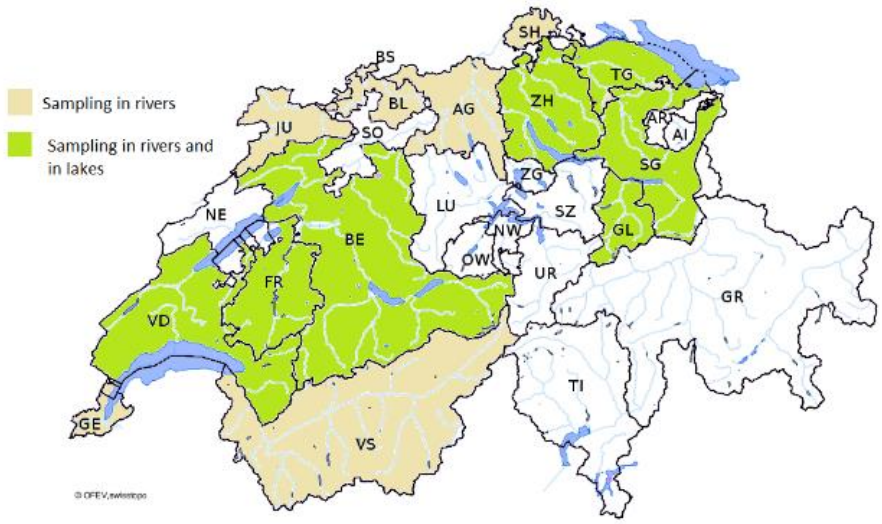

Figure 2: Cantons that monitor sediment quality in Switzerland.

Overall, sediment assessment is mainly carried out by cantonal agencies to monitor point sources or accidental pollution, and to complement the assessment of water quality.

Four cantons have already established a sediment monitoring network. The other cantons choose their sampling sites according to specific environmental objectives or known environmental issues.

Overall, there is a lack of harmonization between cantonal methodologies used in sampling and sample analysis as well as sediment quality assessment in general. In the absence of harmonized recommendations for sediment sampling, sample preparation and chemical analyses, a situation analysis performed in 2012 showed great heterogeneity in terms of sediment fraction and extraction techniques considered for trace metal quantification (Casado-Martinez et al. 2016). Only the cantons of Bern, Basel-Land and Jura have already harmonized their sediment monitoring methods and have had a common standardized protocol for sediment sampling since 2006.

The compounds targeted by most cantons are trace metals and, to a lesser extent, PAHs and PCBs, although some cantons have also considered other groups of substances like pesticides and PBDEs. Other compounds that cantons consider important for sediment monitoring include pesticides (pyrethroids), organotin compounds and surfactants, but these are only considered at specific sites to answer specific questions.

The most common methodology used for the monitoring of trace metal concentrations in sediment is the collection of a composite field sample that is wet sieved at 63 µm with site water, and extracted with *aqua regia* (HNO_3 + HCl). Complementary measurements required for data interpretation such as organic carbon content and grain size distribution are not often measured, which might pose problems for normalization of chemical concentrations and risk assessment.

3.2. Situation analysis of sediment quality

3.2.1. Trace metals

According to a situation analysis performed in 2012, trace metal concentrations in Swiss sediments range from one order of magnitude for Hg, two orders of magnitude for Cd, Cr, Ni and Zn, to three orders of magnitude for Cu and Pb (Table 1). Most data referred to the fine sediment fraction (grain size fraction < 63 µm) and, to a much lesser extent, to whole sediments (sediment fraction < 2 mm), with a non-negligible percentage of data (6%) of unknown grain size. Similarly, almost half of the total number of entries were data obtained using microwave extraction with a mixture of HCl and HNO_3 or *aqua regia*, and the remaining entries did not refer to the extraction methodology used. Most often, these correspond to microwave extraction with H_2O_2 and HNO_3, which yield results similar to those of *aqua regia* (see Box 3).

The comparison of the measured metal concentrations with existing sediment quality guidelines (TEC: threshold effect concentration, PEC: probable effect concentration (MacDonald et al. 2000); Box 1) showed that the order of metals with a higher proportion of entries above probable effect concentrations for benthic invertebrates, indicating high concern, was, in decreasing order, as follows: Ni > Zn > Pb ~ Cu > Hg ~ Cr > Cd. The order of metals, in decreasing order, with the highest proportion of entries below the threshold effect concentrations for benthic invertebrates, indicating low concern, was as follows: Cd > Hg > Pb > Zn ~ Cr ~ Cu > Ni. These percentages are in some way an overestimation because the TEC and PEC are derived for whole sediments (grain size < 2 mm) while most data referred to fine sediments, which tend to concentrate higher concentrations of pollutants. Complementary data (e.g. grain size distribution) are not available to normalize the measured concentrations, making a comparison among these two fractions impossible.

The spatial coverage of available data was patchy, with an apparently random distribution of sites with concentrations of concern (exceeding the respective PEC). This suggests that the sites correspond to hot spots associated with anthropogenic sources rather than relatively high natural background concentrations associated with regional geochemical features. A high ratio between

percentile 90% / 10% of measured concentrations indicates anthropogenic pollution (hot spots). Hg and Pb showed the highest ratios whereas Cr and Ni showed much lower ones. A high incidence of concentrations of concern for Ni (concentrations above the PEC) was located in canton Geneva. Although an overrepresentation of Ni-contaminated sites in this canton could not be excluded due to different study objectives, the high incidence of exceedance of indicative values for soils in this canton was also observed by the "Réseau d'observation des sols Genevois" (GEOS; Lamy et al. 2014). Natural background as a contributing factor to the total Ni concentrations in Geneva and other cantons is therefore not excluded.

Table 1: Descriptive statistics of sediment metal concentrations in Switzerland (1990-2011). Data refer most often to the fine fraction (fraction < 63 µm) and to a lesser extent to total sediment (fraction < 2 mm). The TEC and PEC are derived for total sediment (fraction < 2 mm; Box 1). All data expressed as mg/kg dry weight. MEC: measured concentration; LOD: method detection limit. From: Casado-Martinez et al. 2016

	Cr	Ni	Cu	Zn	Cd	Hg	Pb
Number of entries	488	607	607	593	498	559	592
% samples MEC < LOD	0	0	0	0	13	5	0
Mean	55.3	41.4	60.3	209	0.55	0.25	55.8
Standard Deviation	26.7	31.1	70.0	251	2.25	0.68	81.7
Coefficient of Variation	0.48	0.75	1.16	1.20	4.09	2.72	1.43
Minimum	7.40	5.00	1.30	13.3	LOD	LOD	4.64
10^{th} percentile	31.5	20.5	18.9	68.9	0.15	0.04	14.4
Median	49.5	34.2	42.0	148	0.38	0.12	36.0
90^{th} percentile	86.0	63.4	113	378	0.78	0.41	103
Maximum	247	303	1068	3658	50.0	7.80	1287
Normal distribution [(a)]	No	No	No	No	No	No	No
90^{th} percentile / 10^{th} percentile	2.73	3.09	5.98	5.49	5.20	10.3	7.15
Threshold Effect Concentration (TEC)	43.4	22.7	31.6	121	0.99	0.18	35.8
Probable Effect Concentration (PEC)	111	48.6	149	459	4.98	1.06	128
% samples MEC < TEC	35	15	33	38	95	71	51
% samples TEC < MEC < PEC	62	66	61	55	5	26	43
% samples MEC > PEC	3	20	6	7	1	3	6

[(a)] Shapiro Test, $p<0.001$.

3.2.2. Polychlorinated biphenyles (PCBs)

Regarding PCBs, the reviews on PCB data in Swiss waters (Schmid et al. 2010; Zennegg et al. 2016a; AWEL 2018; Loizeau et al. 2017) showed that PCB concentrations in sediments varied over up to four orders of magnitude, depending on the PCB congener (Table 2). More than half of the entries for the sum of indicator PCB congeners (6 i-PCBs) reported concentrations above the median for Alpine lakes in Tessin (3.54 µg/kg d.w., n=14), which is considered as the reference concentration of pristine sites (Schmid et al. 2010). A slightly higher proportion of samples

(66%) were below 10 µg/kg dw, which was defined as a threshold concentration to consider sediments as slightly contaminated (Zennegg et al. 2016a). An additional 10% of entries had concentrations above typical concentrations at sites affected by diffuse sources (20 µg/kg dw, Zennegg et al. 2016a).

In terms of individual PCB congeners, approximately half of the sites have concentrations above the concentration in Alpine lakes and above toxicity thresholds for effects in benthic invertebrates (Box 1; de Deckere et al. 2011). As for metals, the threshold values derived from ecotoxicological and/or biological studies (Consensus 1 and Consensus 2) refer to total sediment (grain size < 2 mm) whereas most of the data were obtained from the fine fraction, which tends to present higher concentrations of contaminants. Data dispersion suggests that all congeners are present at relatively high concentrations. The Birs (site Choindez), Lake Geneva (at the Vidy Bay), the Limmat (site Ennetturgi), the Glatt and small rivers in canton Zurich (14 sites) present concentrations ten times higher than the median at Alpine lakes.

Table 2: Descriptive statistics of sediment PCB concentrations in Switzerland. Data is provided for the congeners most often quantified in Switzerland (6 i-PCB and 7 i-PCB), and the two congeners used as individual indicators (PCB 153 and PCB 118). Data refer most often to the fine fraction (fraction < 63 µm) and, to a lesser extent, to total sediment (fraction < 2 mm). The threshold values –Consensus 1 and 2- are derived for total sediment (fraction < 2 mm; Box 1). All concentrations expressed as µg/kg dry weight. MEC: measured concentration; LOD: method detection limit.

	PCB 118	**PCB 153**	**6 i-PCB**	**7 i-PCB**
Number of measurements	328	406	406	328
% samples MEC < LOD	38	13	12	42
Mean	1.96	3.26	9.50	14.5
Standard Derivation	5.37	7.15	17.7	25.6
Coefficient of Variation	2.74	2.19	1.87	1.77
Minimum	0.07	0.03	0.15	0.29
10^{th} percentile	0.26	0.29	1.17	1.45
Median	1.00	1.92	5.53	7.85
90^{th} percentile	3.42	6.00	19.7	29.1
Maximum	72.7	118	273	287
Normal distribution [(a)]	No	No	No	No
90^{th} percentile / 10^{th} percentile	13	21	17	20
Threshold effect concentration Consensus 1	0.43	1.5	-	-
Probable effect concentration Consensus 2	6.9	9.7	-	-
% samples MEC < Consensus 1	49	47	-	-
% samples Consensus 1 < MEC < Consensus 2	49	48	-	-
% samples MEC > Consensus 2	2.1	4.9	-	-
% samples MEC > median Alpin lakes	44	67	58	41

[(a)] Test de Shapiro, p<0.001.

Box 1: Sediment quality guidelines (SQGs) available for sediment quality assessment

Types of guideline	Substance considered	Type of sediment	Protection goal	Context /derivation method	Type of data used in derivation [a]				Use of assessment factors to account for uncertainty	Referece
					Ecotoxicology	Ecology	EqP	Other		
Threshold Effect Concentration (TEC), Probable Effect Concentration (PEC)[b]	ΣPCBs, individual and ΣPAHs, metals, organochlorine pesticides	Dry sediment (≤2 mm, 1 % TOC)	Protection of benthic organisms	Sediment quality assessment in US; consensus (geometric mean of existing SQGs)	✓	✓	✓	✓		MacDonald et al. (2000)
Consensus 1 (effect threshold), Consensus 2 (probable effect threshold) [b]	Individual and $\sum_{10}$ PCBs, individual and $\sum_{6\text{-Borneff}}$ PAHs, metals, DDD, DDE, hexachlorobenzene, extractable organohalogenes, non-polar hydrocarbons	Dry sediment (≤2 mm, 5 % TOC)	Protection of benthic organisms	Sediment quality assessment in Flanders; consensus (geometric mean of ecological and ecotoxicological thresholds from Flemish sediment database)	✓	✓				de Deckere et al. (2011)
Environmental Quality Standard for sediments (EQS_{sed}) [c]	Priority substances and other substances depending on country/river basin	Dry weight whole sediment (≤2 mm, most often 5% TOC)	Protection of benthic organisms	EU Water Framework Directive; derivation EU TGD (2011, 2018)	✓	✓	(✓)	(✓)	✓	EC (2011, 2018)
Target Value (TV), ICPR [d]	$\sum_{7\text{-indicator}}$ PCBs, PCB 153, benzo(a)pyrene, metals, hexachlorobenzene	Used for suspended matter and fine sediment	Protection of benthic organisms / ecosystems	Mostly temporal and spatial trend analysis; derivation moving to EU WFD (EU TGD 2011, 2018)	(✓)	(✓)	(✓)	(✓)	(✓)	ICPR (2009)
Quality Standard for sediments for protection of human health from fish consumption ($QS_{hum.cons.}$) [e]	$\sum_{6\text{-indicator}}$ PCBs, Hg, $\sum_{6\text{-indicator}}$ PBDEs, PFOS and hexabromocyclododecane	Dry weight whole sediment (≤2 mm)	Human health	Expert report, not enforced as regulatory EQS; simple bioaccumulation / biomagnification model				✓		Babut (2018)
Interim Sediment Quality Guidelines (ISQGs)	PCBs (total and Aroclor 1254), PAHs, metals, organochlorine pesticides, PCDD/Fs, nonylphenols and ethoxylates, toxaphene	Dry weight whole sediment (≤2 mm, 1% TOC)	Protection of benthic organisms	Sediment quality assessment in Canada	✓	✓	(✓)			CCME (2021)

[a]) In parentheses, approaches used when no effect data is available (e.g. Equilibrium Partitioning –EqP- for EQS_{sed} derivation) or used depending on substance type (TV).
[b] Concentrations above the PEC / Consensus 2 pose a likely risk to benthic communities, while concentrations below the TEC / Consensus 1 pose no risk to benthic invertebrate communities.
[c] The derivation method depends on the available data. More information on the EqP and the derivation of EQS_{sed} in Annex 3.
[d] The derivation method depends on the substance. For organic substances, generally EqP. The ICPR moves towards the WFD EQS_{sed} derivation method.
[e] Uses empirical data from simple models of bioaccumulation and biomagnification. Empirical data on accumulation in sediment, macroinvertebrates and fish.

3.2.3. Conclusions of the situation analysis

From this situation analysis the following conclusions can be drawn:

- The different objectives and strategies (selection of sampling sites, sampling and processing protocols) among cantonal databases make it difficult to provide a concise picture of sediment quality at a pan-national level. A harmonization of sampling and sample processing protocols is advisable.

- For the metals most commonly targeted in sediment quality assessment by cantonal agencies, the situation analysis shows that the vast majority of the measurements for Cd and Hg indicate good sediment quality that are at levels considered safe for the benthic communities (concentrations of low concern). For Pb, Zn and Cu, most measurements are in the range of intermediate quality, with a remaining 6-7% of concentrations above the level of probable effects in benthic communities (highest concern). The most problematic metal is Ni, which is present at medium-high concentrations when compared with existing sediment quality guidelines, although it is likely that these high concentrations are associated with a relatively high natural background in Swiss sediments rather than anthropogenic sources of pollution.

- For PCBs, approx. 50% of the measurements of concentrations are above the environmental levels in Alpine lakes, where there are no direct pollution sources. The 2-5% of the measurements are above the concentrations of probable effects in benthic communities (>PEC, Consensus 2, levels of highest concern).

- A situation analysis for other types of organic micropollutants present in Swiss water bodies such as pesticides, human and veterinary medicines or industrial chemicals cannot be performed because measurement campaigns have been only performed occasionally or have not been implemented at all. As it is known that these type of substances do occur in the environment, a prioritization exercise using alternative indicators of exposure, hazard and risk, as presented in the next chapter, is necessary.

4. Substances proposed for sediment monitoring

It is a fact that, due to technical and economic reasons, it is not feasible to monitor the myriad of chemical substances that may accumulate in sediments. In the context of providing recommendations for sediment quality assessment strategies in Switzerland, 20 substances are selected for which information on measured environmental concentrations in sediments and a risk assessment at the national level is recommended. This list of substances is selected taking into consideration the results of the situation analysis of sediment quality in Switzerland for metals and PCBs and a prioritization exercise to identify other substances for which monitoring in sediments is recommended according to alternative exposure, hazard and risk indicators.

4.1. Prioritization of organic micropollutants

The prioritization of substances for the sediment compartment was carried out in several steps[9] (for the full description see Casado-Martinez et al. 2018):

1) Identification of candidate substances. More than 1000 substances possibly relevant for Switzerland were identified, including authorized plant protection products and biocides (Wittmer et al. 2014), compounds detected in urban waste water effluents (Götz et al. 2010), substances listed in the Swiss Contaminated Sites Ordinance (CSO) and those in the Swiss Pollutant Release and Transfer Register (SwissPRTR).

2) Identification of sediment relevant substances. In total, 240 substances were considered relevant for the sediment compartment according to substance properties (hydrophobicity expressed as log K_{ow} ≥3 or log K_{oc} ≥3 and persistence expressed as the half-life (DT_{50}) in soil ≥40 days) or proven occurrence (previously measured in sediments).

3) Ranking of substances. The 240 substances considered potentially relevant for sediment monitoring in Switzerland were ranked according to exposure, hazard and risk scores. Exposure was assessed, where available, according to demonstrated occurrence in sediments and present use. Hazard assessment was based on substance properties (persistence, bioaccumulation, biomagnification, toxicity and endocrine disrupting potential). Risk potential was based on the traditional risk assessment paradigm that divides measured environmental concentrations by existing environmental quality standards for the sediment compartment in the EU or estimated from existing criteria for surface waters in Switzerland. The risk score was multiplied by a factor of two to give additional weight to proven evidence of risk in the assessment compared to the other two indicators, exposure and hazard.

4) Development of a list of priority substances. See Chapter 4.2.

[9] The screening approach was largely based on the NORMAN (network of reference laboratories, research centers and related organizations for monitoring emerging environmental substances) system. See: https://www.norman-network.net/

4.2. Selection of substances recommended for sediment monitoring

The twenty contaminants proposed for sediment monitoring in Switzerland were selected taking into consideration:

- The ranking in the prioritization.
- The main sources of pollution in Switzerland.
- Their occurrence at ecotoxicologically relevant concentrations and/or their tendency to accumulate in benthic organisms and/or magnify along the food chains.
- The possibility to analyze the proposed list of substances easily with one or two analytical techniques.

The final list of substances proposed for sediment monitoring is presented in Table 3. This list should not be considered as applicable to all cases and can be refined according to the type of water body, the sources of contamination present, and the study objectives.

It should be noted that the list of substances proposed for sediment monitoring could be updated in the future if new data of measured environmental concentrations in sediments points to a low risk at the national level and concentrations are decreasing over time or if the substance is banned in Switzerland. Conversely, new substances could be added to the list if there is evidence that the substance may pose a risk at the national level or if concentrations increase over time.

Table 3: List of substances proposed for sediment monitoring. NA: non-applicable.

CAS	Substance	Type
330-54-1	Diuron	Herbicide
2921-88-2	Chlorpyrifos	Insecticide
52315-07-8	Cypermethrin	Insecticide
107534-96-3	Tebuconazole	Fungicide
85721-33-1	Ciprofloxacin	Antibiotic
50-28-2 53-16-7 57-63-6	E2 [(a)] E1 EE2	Hormones
3380-34-5	Triclosan	Bactericide
NA	PBDE [(b)] (8 indicator)	Organobromines
1763-23-1	PFOS [(c)]	Fluorosurfactant
117-81-7	DEHP [(d)]	Phtalate
NA	Nonylphenols	Phenols
NA	Octylphenols	Phenols
21145-77-7	Tonalide	Synthetic musk
87-68-3	HCBD [(e)]	Halogenated aliphatic compound
NA	HAP [(f)] (16 indicators)	Polycyclic aromatic hydrocarbons
NA	PCB [(g)] (7 indicators)	Polychlorinated biphenyls
7440-50-8	Cu	Trace metal
7440-66-6	Zn	Trace metal
7439-97-6	Hg	Trace metal
7439-92-1	Pb	Trace metal

[(a)] E2: Estradiol-17beta, E1: Estrone, EE2: Ethynylestradiol-17alpha.

[(b)] Polybrominated diphenyl ethers, including: 41318-75-6 (BDE28), 5436-43-1 (BDE47), 60348-60-9 (BDE99), 189084-64-8 (BDE100), 68631-49-2 (BDE153), 207122-15-4 (BDE154), 207122-16-5 (BDE183), 1163-19-5 (BDE209).

[(c)] Perfluorooctane sulfonate.

[(d)] Bis (2-ethylhexyl) phthalate.

[(e)] Hexachlorobutadiene.

[(f)] 16 EPA polycyclic aromatic hydrocarbons, including: 91-20-3 (naphthalene), 208-96-8 (acenaphthylene), 83-32-9 (acenaphthene), 86-73-7 (fluorene), 85-01-8 (phenanthrene), 120-12-7 (anthracene), 129-00-0 (pyrene), 206-44-0 (fluoranthene), 218-01-9 (chrysene), 56-55-3 (benz[a]anthracene), 207-08-9 (benzo[k]fluoranthene), 205-99-2 (benzo[b]fluoranthene), 50-32-8 (benzo[a]pyrene), 191-24-2 (benzo[ghi]perylene), 53-70-3 (dibenz[a,h]anthracene), 193-39-5 (Indeno[1,2,3-cd]pyrene).

[(g)] Including: 7012-37-5 (PCB28), 35693-99-3 (PCB52), 37680-73-2 (PCB101), 35065-28-2 (PCB138), 35065-27-1 (PCB153), 35065-29-3 (PCB180), 31508-00-6 (PCB118).

5. Study design and sampling strategy

This chapter presents the proposed study design, including the definition of the study objectives, the preparation of the sampling strategy, recommendations for the implementation of the field campaign and the description of sediment collection and handling, and recommendations for the analysis of chemicals to be monitored. The detailed sampling strategy included here is suitable for wadeable streams and other small surface water courses, and includes the elements listed in Figure 3.

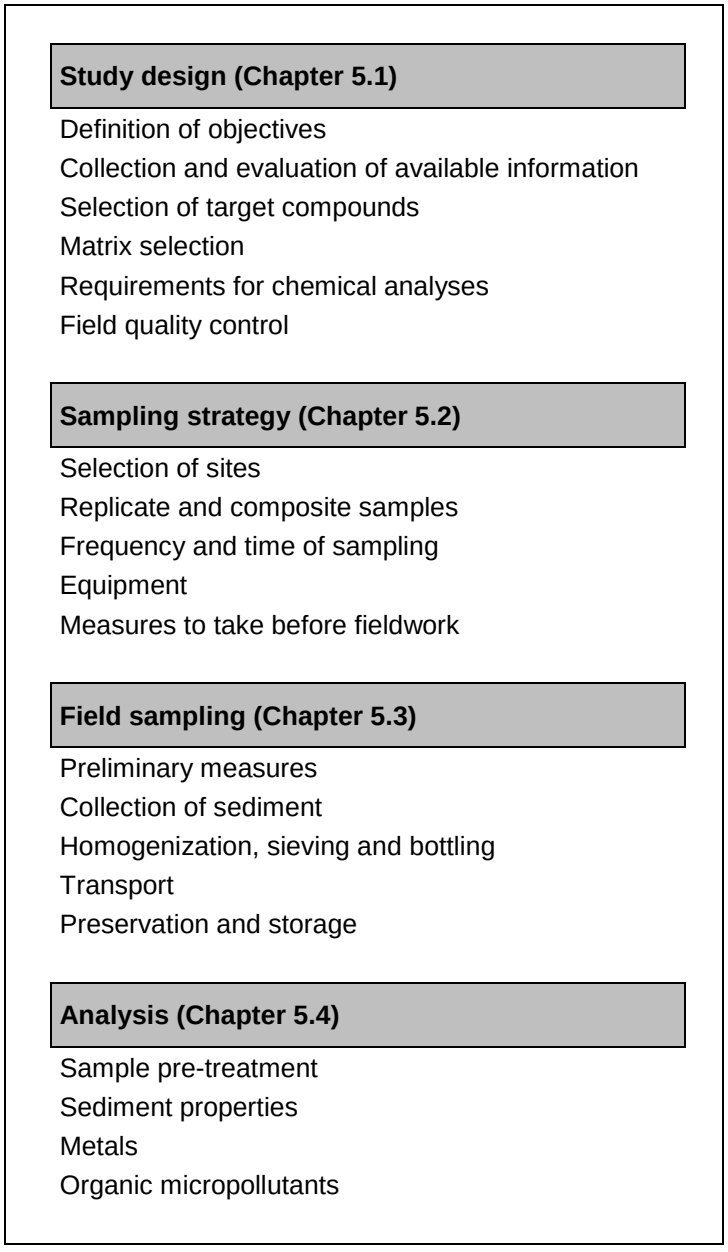

Figure 3: Components of the sampling design, the sampling strategy and analysis as described in Chapter 5.

5.1. Study design

5.1.1. Definition of study objectives

The study design will depend on the study objectives and the research questions that need to be answered according to Table 4.

Four different objectives have been identified for sediment quality assessment in Switzerland:

1. **Monitoring of sediment quality**, for example for obtaining an overview of the potential impact of sediment quality on benthic organisms on the cantonal or regional scale. This is most commonly the objective when no previous information on sediment quality is available or when seeking an indication of potential biological impacts due to sediment contamination.
2. **Identifying the causes of a known ecological impairment,** for example a bad score in the modular stepwise procedure modules[10].
3. **Assessment and monitoring of potential ecological impairment** at known hot spots (for example a contaminated site) for purposes of remediation planning and success control.
4. **Trend monitoring** for identifying spatial and temporal trends of sediment contamination.

5.1.2. Collection and evaluation of available information

After defining the objectives of the study, it is necessary to collect and assess all available information related to the objectives and the water body being assessed. If possible, the following information should be considered:

- Known or suspected sources of contamination, including past contamination and pollution sources upstream (for example, data about domestic and industrial wastewater treatments, descriptions of the surrounding area and soil uses, including soil contamination).
- Data on sediment and water quality or description of effects already observed.

This information can be useful at different stages of the assessment. Available information can serve, as well, to delimit the study area and to identify potential sampling sites, the most suitable sampling equipment and other important points such as the number of people required as well as health and safety precautions. Otherwise, a preliminary field survey may be required.

[10] Modules of the Modular Stepwise Procedure for assessing the quality of invertebrate communities, water plants or fishes.

Table 4: Recommendations for the selection of the study design according to study objectives and sediment properties.

<table>
<tr><th colspan="3">Objective</th><th>Monitoring of sediment quality</th><th>Identification of causes of ecological impairment</th><th>Assessment and monitoring ecological impairment at identified hot spots</th><th>Trend monitoring</th></tr>
<tr><td colspan="3">Problems to solve</td><td>1) Evaluation of potential impacts in benthic organisms on cantonal or regional scale
2) Find indication of biological impact due to sediment contamination
2) Find indication of biological impact due to sediment contamination</td><td>Test for contribution of sediments to known ecological impairment (e.g. bad score in Modular Stepwise Procedure modules)</td><td>1) Monitor the impact at identified hot spots (e.g. point-sources or known discharges)
2) Remediation planning and success control</td><td>1) Identify spatial and temporal trends of sediment contamination
2) Prioritize sites based on chemical contamination</td></tr>
<tr><td colspan="3">Type of assessment</td><td colspan="3">Ecotoxicological</td><td>Chemical</td></tr>
<tr><td rowspan="4">Matrix for analysis</td><td rowspan="4">% sediment <63 µm in 2 mm fraction</td><td>< 5%</td><td colspan="4">Assessment not recommended [a]</td></tr>
<tr><td>< 20%</td><td colspan="3" rowspan="3">< 2 mm</td><td>< 63 µm</td></tr>
<tr><td>20-80%</td><td>(< 63 µm ou) 2 mm [b]</td></tr>
<tr><td>> 80%</td><td>< 2 mm [c]</td></tr>
<tr><td colspan="3">Evaluation</td><td colspan="3">Classification of sediments into 5 classes through comparison with SQC</td><td>Classification by comparison with SQC or other established thresholds [d]</td></tr>
</table>

[a] Sampling sites for sediment monitoring should ideally have more than 5% fine fraction (<63 µm) (EC 2010).
[b] The fraction <2 mm can already identify point sources of pollution and spatial trends in sediment contamination when the sediment contains at least 20% fines (< 63 µm), but this may not hold true of all instances.
[c] According to the results from field trials for sites that have a high proportion of fines, the measurements are representative for the entire matrix, and hence results can be used for comparison to SQC.
[d] For non-ionic substances SQC are normalized for organic carbon content, accounting for the matrix effect on bioavailability to some extent. Otherwise, measured concentration values have to be compared with established thresholds from older measurements in the region or alternative thresholds values (Chapter 6).

5.1.3. Selection of target compounds

Target compounds should be selected on a case-by-case basis to meet the study objectives. If no specific set of compounds has been identified, then target compounds should be selected taking into account the relevant sources of pollution at the study site and existing information gathered in the preliminary survey. The list of substances proposed for sediment monitoring (Chapter 4) covers the most important pollution sources in Switzerland and can be used as is or adapted based on site-specific considerations.

5.1.4. Matrix selection

The method described here is designed to assess the quality of bed sediments using ecotoxicologically-based environmental quality criteria SQC. Taking into consideration that SQC are derived using effect data from the < 2 mm fraction of sediment samples, the ecotoxicologically relevant matrix for sediment risk assessment is the < 2 mm sediment fraction. Therefore, in most cases a < 2 mm sediment fraction should be analysed.

In the course of this project, it became clear that a single methodology would not suit all the assessment objectives for all types of water bodies in Switzerland. There are cases in which analysis of the < 2 mm sediment fraction may not be suitable, depending on study objectives and the nature of the sediment matrix (Table 4). If the purpose of sediment monitoring is trend analysis and the proportion of fine sediments is relatively low, the matrix recommended for analysis is the fine fraction (< 63 µm). In general, focusing on areas of fine sediment or performing the analyses on the fine fraction will increase the statistical power to detect spatial and long-term temporal changes and reduce sampling effort[11].

5.1.5. Requirements for chemical analysis

When designing the study, it is advisable to contact the laboratory performing the chemical analyses to ensure analytical techniques are suitable to meet the objectives of the study (e.g. comparison with SQC) and to define the required sample volume.

5.1.6. Field quality control

Collection of field quality control samples is recommended during sediment sampling. The most important types of quality control samples are summarized in Table 5. The type and frequency of sample collection for quality control should be specified in the study design according to the target

[11] In general, sediments with a low proportion of fines show higher random variability, requiring a higher number of samples to detect statistically significant trends. For in-depth information on how to design appropriate sampling strategies taking into consideration statistical requirements, the reader is referred to the EC WFD Guidance Documents on chemical monitoring (EC 2003, 2009, 2010) and ISO Standard 5667-1 (ISO 2006).

analytes, the expected concentrations in the samples and potential sample contamination (e.g. if sampling in a particularly dirty environment for trace concentrations of analytes, the number of field blanks should be higher than if sampling in a relatively clean environment). The decision to introduce each type of blank samples should be evaluated during the preparation of the study design, taking into account potential bias in the results of the study and the availability of the necessary resources for their collection and processing since the use of blanks will increase the sampling effort and costs of analysis.

Table 5: Types of field quality control samples and quality control objective (adapted from US EPA 1997).

Type of quality control sample	Objective	Pre-treatment
Container blank	To evaluate contamination in sample containers	One of the sample containers is filled with analyte-free water or organic solvent. The blank is analyzed along with the samples collected in the same batch of containers. This type of blank is recommended when containers may contain traces of undesirable substances.
Field blank	To evaluate on-site contamination	An aliquot of analyte-free sample is transferred to one of the sample containers. The blank is analyzed for one or all of the analytes for which associated samples are being analyzed.
Temperature blank	To indicate if appropriate sample temperature was maintained between sample collection and delivery to the analytical laboratory	A plastic container of water is kept in the sample cooler with the batch of samples between sample collection and delivery. The temperature of this water is measured and recorded when samples are received at the analytical laboratory. This type of blank is relevant when temperature may change the concentrations of contaminants in the sediments (e.g. transformation of target compounds).
Field split sample	To measure and document repeatability of sample handling procedures, heterogeneity of the sample matrix, and the standardization of analytical procedures	Twice as much sample is collected, then aliquots are distributed in two sets of containers. This results in two theoretically equivalent samples collected from one sampling location. The field split sample is analyzed for the same set of analytes as the original sample. If the split sample is analyzed by a second laboratory, it documents the standardization of analytical procedures.
Field replicate	To evaluate the repeatability of field sampling methodology and heterogeneity of the sample matrix	A second sample is collected using the same sampling methodology at the same sampling location and as soon after the original sample as possible. The field replicate is analyzed for the same set of analytes as the original sample. N field replicates may be collected at a particular sampling location; statistical analysis of analytical results (mean and standard deviation) estimates the likely range of concentrations at a given location.

5.2. Sampling strategy

After defining the study objectives and the main axes of the study design, it is possible to proceed to the preparation of the sampling strategy. The sampling strategy includes information on the sampling sites, the sampling equipment and materials, the frequency and time of sampling, and the type of samples collected (replicates or composite samples). The sampling strategy should also include a brief description of the project (objectives and research questions) and the data quality objectives.

5.2.1. Site selection

Sampling at multiple sampling sites may be needed to identify the nature, location and magnitude of sediment contamination, with the number and distribution being dependent on the objective of the study. Thus, it is not possible to recommend a single sampling strategy for site selection that can be used in all situations.

Options for selecting sampling sites fall into three categories: random sampling, stratified random sampling and targeted sampling:

- **Random sampling**, in which samples are randomly located, is adequate in homogeneous areas or when no information about local conditions is available. This type of sampling strategy provides an unbiased assessment of sediment quality within a water body and is adequate when the objective is the monitoring of sediment quality on cantonal, regional or watershed scales. It is also useful to delineate sediment contamination around known hot spots. Random sampling may not be suitable for rivers and streams where tributaries and local contamination sources are of concern. In such cases, a more systematic or targeted sampling strategy is needed.
- **Stratified random sampling** strategies account for spatial heterogeneity and ensure key sites are not missed. In this type of sampling several homogeneous areas are identified within a larger heterogeneous area, and then samples are collected randomly within each homogeneous area. This type of sampling strategy requires previous knowledge of local conditions and well-defined zones of different sediment types or land uses. It is recommended when the objective of the study is to identify contaminated sediment on a quantitative spatial and temporal scale, for example in order to characterize specific dredging or remediation sites. In the case of an emission (discharge), sampling locations at increasing distances from the point source may be more adequate.
- **Targeted sampling** means that sampling sites are selected based on previous knowledge. It can be quickly and easily implemented and study objectives can be achieved with a limited budget. However, it is only adequate when relatively small-scale conditions are under investigation, when a small number of samples are required, and when reliable previous knowledge about the area, the pollution source or the sediment

contamination problem is available. Targeted sampling should only be used when the objective of the study is to obtain an overview of sediment quality, or when there are time or budget limitations that preclude the implementation of statistical sampling designs.

Whereas these three types of sampling strategies are appropriate for most study objectives, other types of sampling designs may be necessary to deal with the variability of sediment contamination. Annex 1 summarizes different types of sampling designs and provides respective advantages and disadvantages as well as recommendations for implementation for specific situations.

Sampling sites should be selected based on the objectives of the study and the available information collected in a preliminary survey. In general, the following recommendations can be provided (EC 2010; Annex 1, 2):

- To deal with tributaries or point sources, sampling of the receiving water body should occur where complete mixing is ensured.
- If gradients of contamination are expected because of morphological conditions and/or pollution sources, more sampling sites are required.
- When monitoring of a temporal trend is the objective, samples should consistently be taken at the same well-defined sites. This requires exact coordinates and sites where continuous accessibility is ensured.

Because contaminants in sediments are mainly associated with the fine-grained fraction, fine sediments will have higher contaminant concentrations than coarser ones for an area influenced by the same pollution source(s). The preferred sampling points are those with relatively high amounts of fines, i.e. net deposition areas with soft sediments. In rivers and streams, currents are generally stronger than in lakes and thus the central channel contains the least amounts of deposited fine sediment. Fine deposited sediment is more likely to be found where the water flow is low, for example near the bank of the river and in concave stretches (Figure 4). When assessing lakes, fine deposited sediments are more likely to be found away from the inlet of rivers and shores of lakes, where waves and currents are the highest. At pristine lakes, a relatively low number of sampling sites is required in most situations. Sites containing peat, pebbles, rocks, compacted sediments or coarse sand are less suitable. As a rule of thumb, sampling should not take place in areas with less than 5% of fine sediments (EC 2010).

Sampling site records, including site coordinates and maps with appropriate identification of access roads, should be included in the sampling strategy.

5.2.2. Replicate and composite samples

The number of replicate samples to be collected at each site varies on a case-by-case basis according to the size of the site, the type, distribution and concentrations of the contaminants, the

heterogeneity of the sediment, and the desired level of statistical resolution or precision if quantitative statistical comparisons within and among sites are required. In practice, the number of samples collected at each site usually results from a compromise due to the logistics of sample collection and the costs of analyses. Compositing replicate samples into one sample to be analyzed is a cost-effective option that may allow study objectives under budget constraints to be met nonetheless. Under these circumstances, it is recommended to collect sediments at a minimum of three different points per sampling site separated by several meters, ideally one near each river bank and one within the channel (Figure 4). This approach is considered a good compromise to provide quality data with relatively low uncertainty when limited resources are available, if a large area is being sampled, or if large quantities of sediment are needed because different types of analyses (e.g. chemistry, toxicity, bioaccumulation) are performed (US EPA 2001, de Deckere et al. 2000).

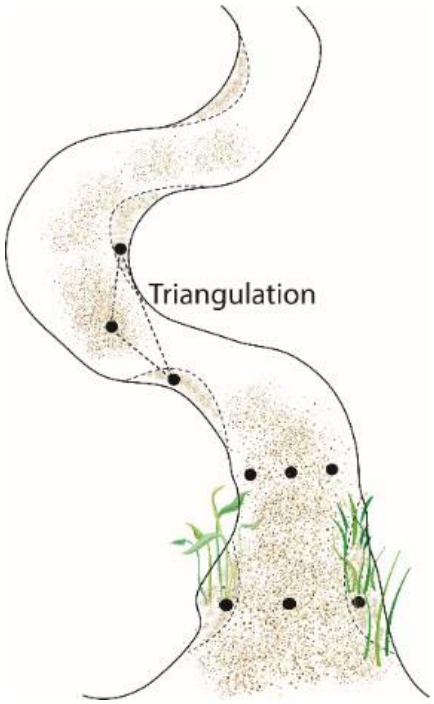

Figure 4: Examples of sediment sampling in at least three different points per sampling site for a composite sample.

Special care should be taken in the case of highly heterogeneous pollution. Pooling of individual samples into one composite sample is not recommended if this could result in dilution of a very localized hot spot. In addition, it is not recommended to mix samples with very different grain size characteristics or when performing power analysis for setting temporal trends programs because such mixing prevents the estimation of field variability, a key parameter for establishing program requirements (EC 2010).

Replicate samples are needed to ensure data quality within any type of study. However, this significantly increases analytical costs. For monitoring programs, field replicates taken at 10% of

the study sites are deemed sufficient for quality control. For regulatory programs or sediment management decision-making, e.g. in the context of dredged material or contaminated sites management, 3-5 replicates per site are recommended. Depending on the target substance, ≤30 – 50 % relative percent difference[12] is used for field replicates as a quality objective (US EPA 2001).

5.2.3. Frequency and time of sampling

Although sediment contamination is temporally not as variable as water quality, sediments are subject to random or systematic variations. In the case of systematic variations (e.g. seasonal), the choice of the sampling time and frequency should capture the entire cycle or at least cover the maximum and minimum values. This is best achieved by systematic and regular sampling schedules.

If the characteristics of the water body do not indicate seasonal variations and sampling is carried out only once a year, sampling should take place at the end of the dry season. For rain-fed water bodies, sampling is recommended at the end of the summer, and for snow-fed water bodies, at the end of winter. This increases the probability of collecting fine sediments. As a rule of thumb, sampling should never take place after an increase of flow that would erode and transport fine sediments (>0.50 m/s; Schiavone and Coquery 2011).

If random inputs of micropollutants or variations in sediment concentrations are predominant, the moment of sampling is less important but an increased sampling frequency is needed to obtain accurate estimates of sediment concentrations over time. It should be noted that the predominant type of variation may be different for different compounds at the same site. In case of doubt, random stratified sampling in time is the best compromise and the number of samples to be taken should allow statistical analysis (EC 2003, 2009, 2010; ISO 2006).

5.2.4. Equipment

There are several types of samplers used for collecting bed sediments, and the selection of one or another type will depend on the accessibility of the site, water depth, the bed material, compounds investigated and the type of investigation and research questions being addressed.

At sites with low water depth such as wadeable streams and bank sediments, the easiest system to use is a scoop or a manual dredge (Figure 5). Scoops are available in plastic or metal, and the selection of the scoop material depends on the chemicals to be analyzed. Plastic should be used when the target compounds are trace metals, while metal should be used when the target compounds are organics. At higher water depths (or when the target matrix is the fine fraction (< 63 µm)), telescopic samplers may be a better option than scoops (Figure 5).

[12] $Relative\ Percent\ Difference\ = \frac{C1-C2}{\frac{C1+C2}{2}} \times 100$

Where C1 is the concentration of analyte from sample 1, C2 is the concentration of analyte from sample 2.

Grab samplers consist of one or more hinged buckets that close while being raised (Figure 5). Grabs are ideal for determining the horizontal distribution of variables in physical, chemical and biological investigations and for assessing recent inputs of pollutants. They are most often used in lakes and large rivers and their usability is relatively limited in small streams and channels. The inner surface of grabs is not inert and, in the case of the van Veen grab, it is metallic, which can contaminate sediments in contact with this inner surface.

Corer samplers consist of a tube that is pushed into the sediment. When pulling the tube out, an undisturbed sediment core is obtained that can be used for determining the vertical distribution of variables, defining strata, and for assessing long-term historical inputs. This system is suitable for physical and chemical investigations as well as limited biological investigations. Its suitability for different types of substrates depends on the specific type of corer used. Gravity and box corers are not suitable in coarse-grain or consolidated sediment but vibrocorers are. Cohesionless fluvial sediments and coarse-grain sediment in general, which cannot be sampled using traditional sampling equipment, can be collected using freeze-core technology. This technique, which involves the freezing of sediments by injecting liquid N or CO_2, is also useful for determining accurately the vertical distribution of contamination independent of the nature of the matrix.

If suspended sediment and sediment deposition is the target of investigation, other methods such as sediment traps and time-integrated suspended sediment tube samplers can be used (Figure 5). Sediment traps passively collect particulate material settling out of the water column over a time period. They can be simply open buckets of a given volume that are filled with cleaned gravel and immersed in the streambed. They have been used extensively for decades to study particle fluxes and composition in lacustrine environments, and they are suitable for physical, chemical and biological analyses. Time-integrated suspended sediment tube samplers are suitable for collecting time-integrated suspended sediments in running streams and can be easily constructed and deployed (Phillips et al. 2000). For other types of instrumentation addressing different types of bed material, bed topography and water quality, see US Geological Survey Federal Interagency Sedimentation Project (FISP)[13].

[13] https://water.usgs.gov/fisp/catalog_index.html

Figure 5: Different sampling devices that can be used in the field. A) Telescopic sampler B) Ekman grab sampler C) Time-integrated suspended tube sampler D) Scoop.

5.2.5. Measures to take before the field work

Safety measures

The following tasks have to be addressed before going into the field. They are important for the safety of the operators and the appropriate implementation of the sampling campaign:

- For safety reasons, at least two people are necessary for sampling.
- **Hydraulic power**: if the flow in the water body or section where the field work takes place is regulated by hydropower dams, the operator of the hydropower facility should be contacted to fix the date and time of sampling according to the exact schedule of flow variations. Sampling should not be carried out unless safety is guaranteed by the hydropower facility operator. Special attention should be paid to automatic installations (e.g. automatic purges).

- **Flood risk**: the operator should inquire about the hydrological[14] and meteorological[15] conditions before each field campaign to assess the risk of flash floods or floods in the streams to be sampled.
- **Risks of contamination of watercourses**: to avoid any transport of pathogens and contamination between watersheds, the operator should disinfect the sampling equipment and boots with a suitable product at each watershed change, when working near a fish farm or when moving upstream from a downstream site.
- **Authorization request**: authorization should be obtained from cantonal authorities.

Preparation of sampling material

A detailed list of materials for sediment sampling is provided in Annex 2A. This list includes personal protective equipment (waders, safety jacket, first aid kit, gloves, etc.), the equipment needed for site characterization (field sheet, GPS, multiparameter probe, etc.), and the tools and materials needed for the collection and homogenization of samples (e.g. sampler, buckets), sieving (spoons, sieves, etc.), transfer (funnel, sample containers) and transport (cold box).

All tools and containers for sampling, transport, pre-treatment and storage have to be prepared in advance. Tools and containers used in every phase of the sampling and pre-treatment of sediments should be selected carefully so that they do not interfere with the target analyses. They should be made from materials that do not contaminate the sample and should be cleaned following appropriate protocols (Table 6).

When organic compounds are targeted, glass and stainless steel should be used in every step. Glass containers are generally recommended for bottling. Polyethylene, polypropylene or polystyrene crystal is preferable for sampling and storing samples for quantification of those elements that are major constituents of glass (e.g. sodium, potassium, boron and silicon) and trace metallic moieties (e.g. mercury). If the material used for sampling is not the adequate for the target analytes (e.g. metallic grabs, PVC corers), the sediment in contact with the sampling equipment should be discarded to avoid risk of contamination.

If both organic and metallic compounds are targeted for the analyses, two separate samples should be taken with different sampling equipment in parallel.

[14] http://www.hydrodaten.admin.ch/f//index.htm
[15] www.meteosuisse.admin.ch

Table 6: Recommendations for selecting sampling and storage equipment materials.

Analysis	Material	Pre-treatment
Metals	Polystyrene crystal or polypropylene containers Polyethylene or Teflon spoons	Sample containers and lids should be: - Thoroughly cleaned with a phosphate-free detergent solution and rinsed with metal-free water. - Soaked for 24 h in acid solution (e.g. 1-2% HNO_3 or HCl) and rinsed with metal-free water.
Grain size	Polystyrene crystal or polypropylene containers	No special treatment.
Organic contaminants, carbonates and organic carbon	Glass jars Stainless steel spoons Aluminum folder	Sample containers should be: - Thoroughly cleaned with a phosphate-free detergent solution, rinsed with water. - For semi-volatile compounds, an acetone rinse with the lid in place. Alternatively, heat glass containers at 350-450°C for 4-8 h. - For volatile organic compounds, avoid solvent rinse because of interference with analysis, although a methanol rinse is acceptable. Then dry at 105 °C. - Store jars in calcified aluminum sheets.
Phthalates	Glass, Teflon, polytetrafluoroethylene, aluminum or steel Plastic material is absolutely prohibited	Sample containers should be: - Prewashed (e.g. phosphate free soap), then washed with an appropriate solvent (e.g. acetone and then purified hexane) or acid solution (e.g. H_2SO_4, HCl). - Then calcified at 400-550° for 4h- to overnight.

5.3. Field sampling

Figure 6 shows the key steps and the measures to be taken in the field, from sediment collection to the pre-treatment of samples upon arrival at the laboratory. See as well a field protocol in Annex 2B.

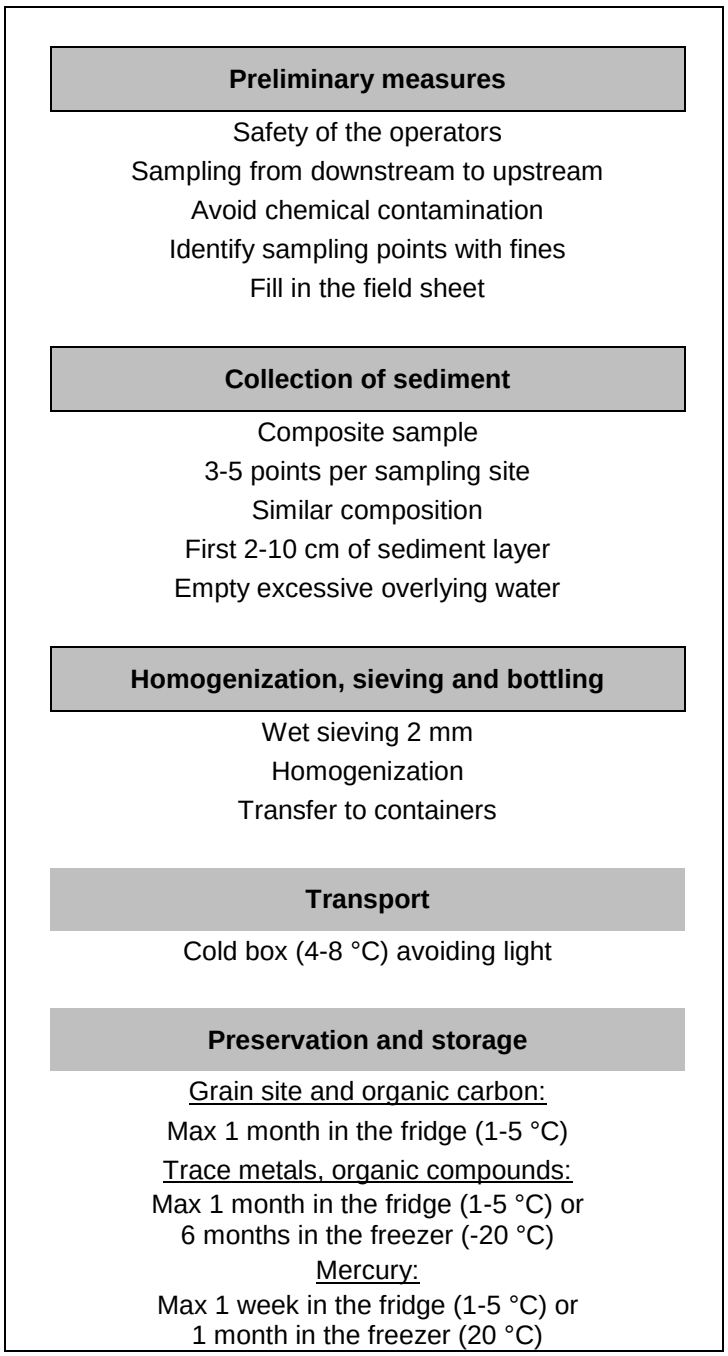

Figure 6 : Key steps and measures to take from field sampling until pre-treatment of samples upon arrival at the laboratory (see text for details).

5.3.1. Preliminary measures

Sampling should always take place in the downstream-to-upstream direction to avoid undesirable effects due to remobilization of the sediment. After taking all necessary measures to avoid chemical contamination of the sampling equipment and samples, it is recommended to prepare all the equipment required for sampling, sieving and storage near the first sampling site (the most downstream section). The water depth, the current and the nature of the substrate at each site should be checked before entering the river.

Because the preferred sampling points are those with relatively high amounts of fines, the percentage of silts and clays in a sample can be roughly estimated in the field by marking a line on a clear jar and then marking 20% of the way up to that line on the jar with another line. Fill the jar to the top line with sediment and vigorously shake the jar and set it aside to settle. A headspace in the jar of 2-3 cm allows for easier mixing. After settling for 10 minutes, an estimate of the particle size distribution can be made with a visual inspection of the sediment stratification in the jar. If the fines stop below the 20% line, then the silt/clay fraction is likely to be <20%.

Field sheets should always be used to ensure all data needed for the interpretation of results is collected at the time of sampling. An example is included in Annex 2C.

It is recommended to measure the following water quality parameters before entering the site: temperature, pH and dissolved oxygen concentration and percent saturation.

5.3.2. Collection of sediment

If possible, sediments should be collected at a minimum of three different points per sampling site separated by several meters to obtain a representative sample of the area. These subsamples will be combined and should ideally be collected near the left bank, near the right bank and in the middle of the channel (Figure 4). If this is not possible, multiple points can be subsampled until enough sediment volume is obtained. The systematic distribution of individual sampling points in a diagonal sense along the stream traced in a targeted manner is the most cost-effective approach (Figure 4).

Sediments should come from areas where they are always submerged.

It is recommended to collect the top 2 to 10 centimeters of sediment. Only those subsamples that have a composition similar to those already sampled (based on visual aspects like color, texture, grain size) should be kept. Samples with obviously different grain size should not be mixed.

It is recommended to discard excessive overlying water before adding the sediment to the sampling container in order to avoid loosing fine particles.

When enough sediment has been collected, it is recommended to manually remove the pebbles, leaves and other branches. Any peculiarities of the sample in terms of color (change of color in contact with air), smell and consistency should be noted on the field data.

5.3.3. Homogenization, sieving and bottling

Homogenization and sieving can be performed either *in situ* or off site (Figure 7). *In situ* sieving has the advantage that the fraction >2 mm can be discarded directly in the field, reducing the volume of sample to transport. After homogenization of the contents of the bucket with an inert spatula, sediments are sieved using a 2 mm mesh size sieve of the appropriate material (Table 6) without addition of extra water, and the sieved sediment is collected in a second bucket.

The sieved sediments are transferred to pre-labeled wide-mouth 500 mL vials, which should be filled to the brim (i.e. no air space). A small amount of water from the site may be added to the vial prior to closure in order to minimize contact of the sediment with air. If the samples will be stored frozen, some free space on the upper side of the container should be kept as samples will expand when frozen.

Figure 7: Example of wet sieving at 2 mm. (A) Off site with inert equipment for trace metal analysis and (B) In situ with inert equipment for organic micropollutant analysis.

If the matrix for analysis is the fine sediment (< 63 µm), wet sieving is recommended with the aid of site water (Figure 8). *In situ* sieving helps to ensure that enough sediment was collected for analyses, and facilitates access to site water needed for wet sieving. If sieving is performed *ex situ*, large quantities of water with suspended sediment must be transported to the laboratory to allow settling and collection of deposited fine sediments.

If it is necessary to perform chemical analyses in the fraction <2 mm as well as in the fine fraction (<63 µm), it is possible to carry out consecutive sieving steps with sieves of the desired mesh size. This can be done *in situ* or in the laboratory. In this case, the difficulty lies with obtaining the appropriate amount of sediment for the target analyses.

Figure 8: Sieving system to isolate the fraction <63 µm (Photo: canton Bern).

5.3.4. Transport and storage

Samples must be transported and stored in a cold box (4-8°C) avoiding light to halt biological activity and to prevent any chemical transformation in the sediments. Transport and pre-storage conditions should be specified on the field sheet.

Preservation, transport and storage methods should ensure that the physico-chemical and structural characteristics of a sediment sample are maintained. The logistics design for sample preservation and transport should be adapted depending on particular constraints of the sampling campaign such as localization of sampling sites (close *vs* distant) and the number and volume of samples and target substances in order to store the sample in appropriate conditions as soon as possible. In general, cooling devices for the transport and storage of samples are not mandatory when measured for total metal concentrations.

The storage conditions and maximum storage duration are specific to the target analyses. According to ISO/DIS 5667-15[16], sediment samples can be stored up to 1 month in the fridge (1-5°C, dark and airtight) for the purpose of analysing grain size distribution, total organic carbon/organic matter, total phosphorus, as well as metals and organic compounds including PCBs, PAHs and pesticides. When total Hg is the target compound, storage duration is limited to one week in the fridge and one month in the freezer.

For metals and organic compounds, storage of samples for up to 6 months in the freezer (-20°C ± 2°C, dark and airtight) or as a dried sample at ambient temperature, dark and airtight is acceptable. Sample glass containers may break during freezing. It is recommended to test the suitability of the containers for freezing wet samples prior to use. In addition, containers should not be filled to the brim to allow sample expansion during freezing.

Alternative preservation and storage conditions may be suitable if the laboratory can prove that there are no losses during the storage period.

Further recommendations for the storage of sediment samples for additional target analyses are provided in ISO/DIS 5667-15.

[16] ISO/DIS 5667-15 Water quality – Sampling – Part 15: Guidance on preservation and handling of sludge and sediment samples.

BOX 2: Validation of sampling methodology

The implementation potential and feasibility of the proposed sampling protocol was evaluated by means of a collaborative sampling exercise that took place from June to November 2016. Eight operators applied the proposed methodology simultaneously at the same site.

Reliability and feasibility of the sampling methodology

The results of the collaborative sampling exercise showed that the proposed protocol was easily implemented by the different operators, and no significant differences were found between the measured sediment metal concentrations of samples taken by different operators, regardless of the familiarity of the operator with the protocol. The resulting intraclass correlation coefficient (ICC; Bartlett and Frost 2008), which is an index for reliability, was 0.84 for a same operator (intra-operator) and 0.77 for different operators (inter-operator). ICC can have values between 0 to 1, with values less than 0.5 indicating poor reliability and higher than 0.9 excellent reliability (Koo and Li 2016; Watson and Petrie 2010). The results showed that the proposed method had good to excellent intra-operator reliability and moderate to good inter-operator reliability. The intra-operator reliability is generally higher than the inter-operator reliability (Bartlett and Frost 2008). Regarding the feasibility of the proposed method, the main difficulty reported by the operators was finding sampling points that contained a sufficient quantity of fine sediment to obtain a composite sample at some of the selected study sites.

Precision and global uncertainty

The precision of the sampling protocol was estimated using the repeatability coefficient (RC) of two repeated measurements performed by a same operator at 13 different sites. The RC represents the precision of the method with 0.95 probability, and is expressed in concentration units. RC ranged between 6.5 mg/kg d.w. for Cr to 20.3 d.w. mg/kg for Cu (Table 7).

Global uncertainty, estimated based on the results of the performance test and expressed as the relative expanded uncertainty, was 18-67% for the sampling step only. Uncertainty, including sampling, extraction and analysis (extraction by *aqua regia* in the microwave and quantification by ICP-MS), was 39-103% (95% probability). As expected, variability depended strongly on the level of sediment metal concentration and the type of substrate at the study site.

Uncertainty associated with the sampling must be considered for the interpretation of results, especially when concentration values are compared with SQC (Ramsey and Argyraki 1997). To deal with uncertainty, it is recommended to include field replicates at an appropriate number of stations to estimate sampling uncertainty as well as analysis replicates to estimate measurement uncertainty.

Table 7: Repeatability coefficient (RC) of the proposed sampling protocol for one single operator at 13 sites.

	Cr	Cu	Ni	Pb
RC ± SE (mg/kg)	6.4 ± 2.3	20.3 ± 7.3	12.5 ± 4.5	9.3 ± 3.4
Range of applicability (mg/kg)	14.7-86.5	9.5-78.5	9.9-49.7	7-40.5

Table 8: Uncertainty (expressed as relative expanded uncertainty, in %) associated with the sampling step and global uncertainty, including extraction and analysis.

	Cd	Co	Cr	Cu	Pb	Zn
Sampling U'	23	30	67	27	18	23
Global (Sampling + Extraction + Analysis) U'	39	46	103	48	43	47

5.3.5. Sample pre-treatment

Sediment samples should be pre-treated differently depending on the target analyses before the end of the maximum storage duration:

- Total Organic Carbon (TOC) and dry mass: drying a subsample of the sediment at 105 °C is used for estimating the dry mass and for subsequent TOC measurement.
- Trace metals: a subsample of sediment is dried at max. 40°C.
- Organic contaminants: sediments should ideally be freeze-dried unless volatile organic compounds are targeted. If freeze-drying is not feasible or available, alternative pre-treatment methods are suitable as soon as it is proven by the laboratory that there are no significant losses during the different pre-treatment steps and QA/QC requirements are met.

5.3.6. Sediment properties

Sediment grain size

A full grain size characterization using hydrometers or laser particle analysis is recommended. If this is not possible, an estimation of the content of fines can be obtained by sieving wet sediment samples pre-sieved at 2 mm through one (63 µm) or several superimposed screens (e.g. 63 µm, 106 µm, 150 µm, 180 µm, 500 µm) with the help of deionized water. Each sediment fraction is then dried and the proportion of each fraction is estimated.

Total organic carbon content (TOC)

Total organic carbon (TOC) can be quantified using automated high-temperature C analyzers (e.g. Shimadzu TOC-V). These analyzers determine TOC as the difference between the total carbon (TC) and inorganic carbon (IC). TC is estimated by combustion of the sample in an oxygen stream with a catalyst (e.g. Tungsten Oxide, Vanadium Pentoxide) at 900°C and IC is determined after acidifying the sample with phosphoric acid at 200°C and bubbling the resulting CO_2 that is produced in the reaction with nitrogen. This procedure has also been recommended for the evaluation of PCB contamination in sediments (Zennegg et al. 2016b).

Alternatively, the loss on ignition (LOI) is a quick and inexpensive estimate of sedimentary organic matter. No standard protocol exists for LOI analysis. Furthermore, LOI is affected by ignition temperature, duration of ignition and ignited sample mass. For harmonization, ignition of 2 g of sample pre-dried at 105°C at 550°C for 4 hours is recommended (according to Heiri et al., 2001).

LOI can be converted to TOC either by means of a fixed conversion factor or regression analyses. The use of a single conversion factor to estimate TOC from LOI is discouraged due to the dispersion of data at LOI content between 0.5 and 7.5%. The following equation for total sediment and fine sediment can be used[17]:

[17] Based on results from 80 data pairs of TOC/LOI from Swiss sediments (14 different sites).

Total sediment (2 mm) with a mean prediction error of 57%:

$$TOC_{2mm} = 10^{-0.19} * LOI^{0.79} * 10^{\frac{0.0156}{2}} = 0.635 * LOI^{0.79} * 1.07 \qquad r^2=0.52$$

Fine sediment (63 µm) with a mean prediction error of 11%:

$$TOC_{63\mu m} = 10^{-0.61} * LOI^{1.18} * 10^{\frac{0.062}{2}} = 0.248 * LOI^{1.18} * 1.02 \qquad r^2=0.82$$

As the prediction error can be high (specifically for coarse sediment), it is recommended to perform full TOC analyses at least once to determine the specific LOI/TOC relationship for the site under investigation.

5.3.7. Metals

The analysis of trace metals (except Hg) in sediments consists of a digestion step and the subsequent analysis of elements (Box 3). To attain better comparability of the results between cantons and for the implementation of SQC, extraction with a*qua regia*[18] is recommended given that this acid mixture is the most widely used extraction procedure among cantons and to derive effect data used for SQC development. *Aqua regia* is the preferred digestion method for sediments under the EC WFD (EC 2010) as it is considered a better proxy for the environmentally available metals fraction (US EPA 1996a).

Metal concentrations after extraction with nitric acid and hydrogen peroxide (HNO_3 + H_2O_2) are comparable to those obtained with *aqua regia* when a high pressure microwave is used. Alternative extraction methods are acceptable if the laboratory proves that the results obtained are comparable to those obtained with *aqua regia*. After dilution of the extracts, metals are analyzed by either ICP-MS (Inductively Coupled Plasma Mass Spectrometry) or ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry).

Mercury determination requires alternative methodologies such as CV-AAS (Cold Vapor Atomic Absorption Spectrometry) after thermal decomposition of the sample, most often using an automatic solid analyzer (Aquaref 2013; Szakova et al. 2004; US EPA method 7473: 1998).

[18] *Aqua regia* is a mixture of nitric acid and hydrochloric acid in a molar ratio of 1:3.

BOX 3: Comparison of extraction techniques for the determination of metals

Different digestion methods can be used for subsequent trace metals analysis, ranging from partial extraction with weak acids or chelating agents (Brady et al. 2016) to total rigorous digestion with hydrofluoric acid (HF) or HF in combination with strong acids (Sun et al. 2001). The best extraction technique for estimating the total content of metals in sediments is digestion with HF in combination with strong acids. Although the use of HF in the laboratory has been objectionable, total mineralization with HF is still required for normalization against co-factors based on Li or Al concentrations (ICES 2009; EC 2010). *Aqua regia*, which is called a pseudo-total extraction, is traditionally considered to be a reasonable alternative to HF. To account for bioavailability, several extraction procedures have been proposed such as the BCR three steps extraction (Rauret 1998), a sequential extraction procedure (Maiz et al. 1997; Tessier et al. 1979), and a weak acid extraction with 1 M HCl (Simpson and Spadaro 2011). However, some issues remain in terms of analytical reproducibility and precision, time consumption, comparability of data and quality control (Brady et al. 2016; Rauret 1998; Sun et al., 2001; Tessier et al., 1979).

In Switzerland, different total and pseudo-total extraction techniques are in use. Four of them were compared for the determination of metals from 20 sediment samples (Table 9). The results of this comparison exercise showed that the bias between extraction methodologies is relatively constant although the amplitude of the bias depends on the metal considered. The highest difference between total extraction with HF and pseudo-total extractions was observed for elements with the highest geogenic contribution, such as Cr and Ti, with the OSol extraction showing the lowest concentrations for these metals. The OSol method also showed a lower degree of extractability (15 out of 20 sediments studied) compared to *aqua regia* (relative extractability Cd: 85%, Co: 95%, Cr: 36%, Cu: 92%, Ti: 63%, Zn: 95%, Ni: 96%, Pb: 90%). Metal concentrations obtained after extraction with HNO_3 + H_2O_2 in high pressure microwave and extraction with *aqua regia* were not significantly different.

Table 9: Extraction methods most often used by Swiss laboratories for the determination of metals in sediments.

Method	Acid mixture	Extraction condition	Comments
Total with HF	HF + H_2O_2 + HNO_3	High pressure microwave[(a)]	Not used on a routine basis
Rhine SPM	HNO_3 + H_2O_2	High pressure microwave[(a)]	Method used to monitor metals in suspended particulate matter from the Rhine
OSol modified	HNO_3 2M	Oven[(b)]	Used by some cantonal and other laboratories
Aqua regia	HNO_3 + HCl	Microwave[(c)]	Used by most cantonal laboratories

[(a)] Milestone ultraCLAVE: 10 min 180°C, 4 min 250°C, 10 min 250°C, 120 bar, 1000 W.
[(b)] Time 16h, 100°C.
[(c)] ETHOS 1 Microwave Laborsystem Programm : 10 min 150°C / 5 min 190°C / 35 min 190°C / with 800 W. 15 min 80°C / 5 min 50°C with 100 W.

5.3.8. Organic micropollutants

The analysis of organic pollutants in sediments requires an extraction step, which differs according to the targeted compounds. Then, the extract often requires a cleaning step in order to gain in selectivity by reducing the matrix effect. Afterwards, the clean extract can be injected into the analytical system, which is usually based on gas or liquid chromatography separation techniques, coupled with mass spectrometry techniques for the quantification of the compounds. The analytical methods applied after the extraction and clean-up steps are generally the same as for water samples. A short description of analytical requirements for substances in Chapter 4 is included below[19].

Extraction

Several extraction procedures, mainly using organic solvents, can be used to extract organic compounds from the sediment matrix and are referred to as Solid-Liquid Extraction (SLE). According to the Technical Guidance Document No. 25 on chemical monitoring of sediment and biota under the WFD (EC 2010), the extraction of wet sediment samples requires the use of a first solvent that is miscible with water (acetone), followed by a less polar solvent such as pentane or hexane. This procedure works well for non-polar substances such as organochlorinated pesticides, PAHs, PBDEs and chlorinated benzenes, but special care should be taken with volatile compounds for which extraction of wet samples, where the freeze-drying step is avoided, would be preferable. Alternative extraction methods for volatile compounds use purge-and-trap or head space sorptive extraction techniques (EC 2010).

Soxhlet Extraction (SXE) is a traditional extraction method and is used for the extraction of many persistent organic pollutants that can be found in the sediment compartment: PCBs (US EPA Method 3540C; 1996b), PBDE (US EPA Method 1614A; 2010), etc.

Accelerated Solvent Extraction (ASE) and Pressurized Solvent Extraction (PSE) have become, however, more robust and reproducible methods for the extraction of persistent organic pollutants, but one has to take care of the PCB results in comparison with soxhlet extraction if sediment has a high carbon content (Bandh et al. 2000). Nonetheless, for PAHs in particulate matter, they seem to produce comparable results to SXE or Ultrasonication Extraction (USE) (Heemken et al. 1997). Basically, ASE is a solid-liquid extraction technique with the possibility of applying defined temperature and pressure conditions and, compared with SXE, it has the advantage of using less solvent and being less expensive.

Other extraction techniques are often used for the extraction of organic contaminants from the sediment matrix: Microwave Assisted Solvent Extraction (MASE or MAE), Ultrasonication extraction (USE) or ultrasonic assisted extraction (UAE), superheated water extraction (SHWE), etc.

[19] For other substances not mentioned in the text, the analytical techniques existing at the time of writing can be found in the SQC dossiers of the corresponding substances, available on request (info@centreecotox.ch).

Most laboratories running sediment analyses for organic contaminants in Switzerland use SXE or ASE for the extraction of classical pollutants (PCBs and PAHs).

Cleaning

In order to have better selectivity and reduce the matrix effect, organic extracts require a cleaning step. Indeed, extensive cleanup is required if the samples are likely to contain biological macromolecules, sulfur from reduced conditions and/or oil or grease (EC 2010). Usually, Florisil® (EPA Method 3620; 2010), Silica gel or Alumina are used. In order to remove sulfur present naturally in sediments, an additional cleanup step is often necessary using Cu or tetrabutylammonium (TBA) sulfite (EPA Method 3660B; 1996c). Reversed phase Solid Phase Extraction (SPE) can also be used as a clean-up step according to the target compounds, e.g. for steroid hormones (Omar et al. 2017, Yarahmadi et al. 2018). ASE allows an on-line cleaning by loading the cleaning material into the ASE cell.

Analysis

The recommended detection method for analysis of semi-volatile and volatile organic pollutants in sediment is based on the use of Gas Chromatography coupled with mass spectrometry (GC-MS). The use of selective methods based on GC-MS techniques are recommended for most organic compounds because such analysis can often reduce problems caused by matrix interference (EC 2010). The use of Liquid Chromatography coupled with mass spectrometry (LC-MS) is more recommended for non-volatile organic pollutants such as most of the pesticides and pharmaceuticals.

Methods quality standards

The analytical methods used for the analysis of targeted compounds should be validated for their selectivity, linearity and repeatability according to international quality standards (Thompson et al. 2002). The determination of limits of detection and quantification of the methods can be done in different ways and should therefore be documented. The assessment of method uncertainties, the use of reference materials for the validation of methods, and the participation in Round Robin tests is highly recommended to verify the robustness of the analytical methods (Ellison and Williams 2012; ISO 5725, 1994).

6. Sediment quality assessment

A generic tiered assessment framework is proposed (Figure 9) in which sediment quality criteria are only one of the lines of evidence used for sediment quality assessment (TGD, EC 2011, 2018). Typically, the first level of investigation -Tier 1- involves conservative/worst case assumptions while the second level, Tier 2 involves more realistic assumptions. The goal in progressing from screening to more in-depth assessments is to diminish residual key uncertainties and improve confidence during the decision-making process.

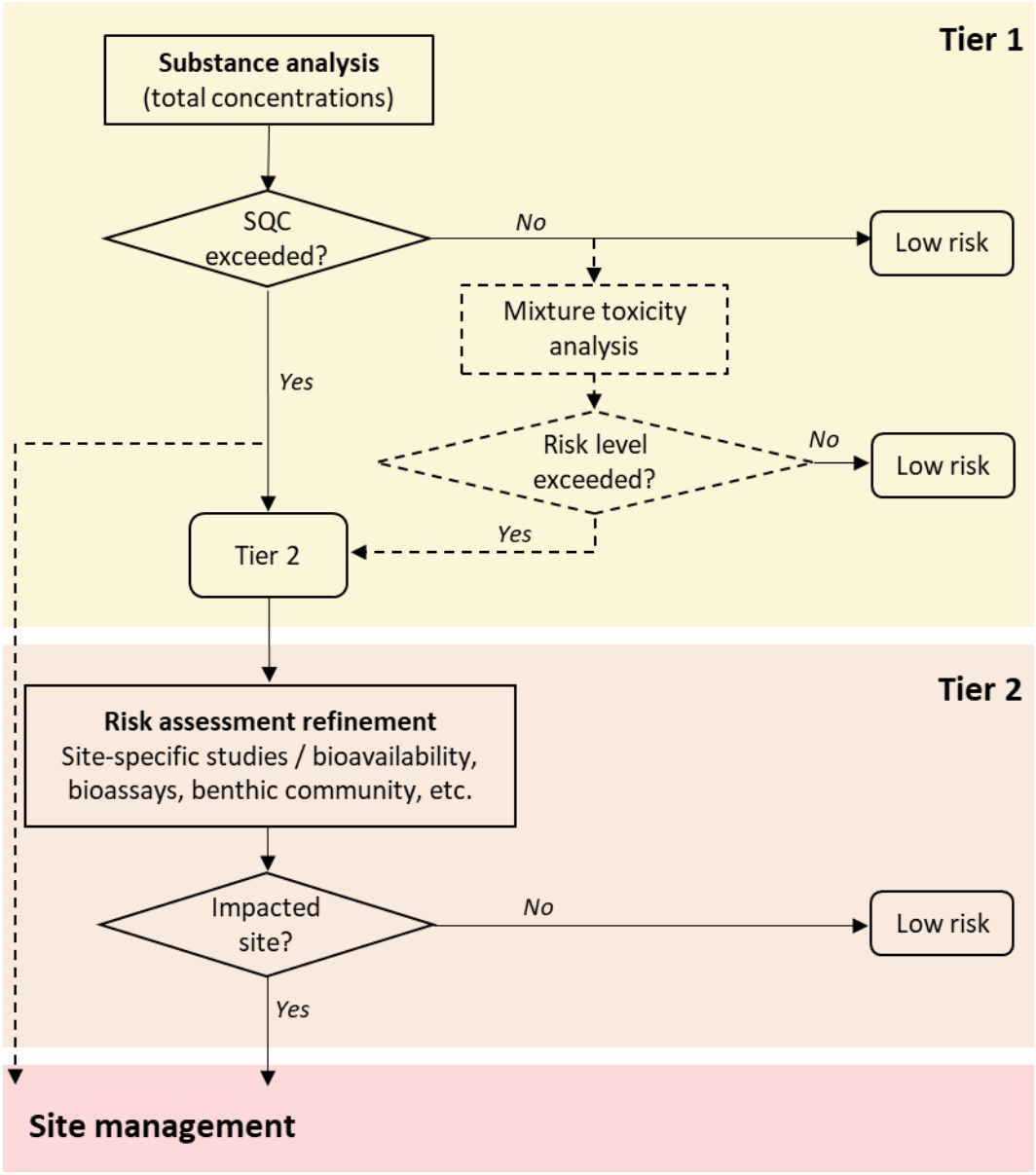

Figure 9: Tiered framework proposed for sediment quality assessment.

The proposed assessment strategy can be used for evaluating sediment chemistry data to identify locations where sediments may be harmful to aquatic organisms. In agreement with current practice in sediment quality assessment worldwide, it is recommended that SQC be employed as screening tools or benchmarks (CCME, 1995; EC, 2010; Simpson et al. 2013; US EPA 2001). Under most circumstances, exceedance of SQC should trigger further investigations to refine the risk assessment or verify the potential risk associated with the exceedance. Indeed, differences in the bioavailability and hence the toxicity of contaminants in different sediment types are likely to occur. In addition, it should be noted that exceeding the SQC does not necessarily signal impairment of the biological community or certify toxicity, but it can no longer be excluded that aquatic organisms are not affected. Conversely, non-exceedance of the SQC does not mean that sediments do not pose a toxic hazard because the number of contaminants analysed is limited and the SQC may not be definitive. In addition, mixture toxicity is complex. Therefore, the potential for observing adverse biological effects as indicated by exceedances of SQC must be evaluated in conjunction with other information (see 6.2). Nevertheless, management measures may be established without conducting further assessments, for example if sediment concentrations greatly exceed the corresponding SQC (dashed arrow on the left of Fig. 9).

Depending on the objectives and problems to solve, the complexity of sediment quality assessment may vary. If the goal of assessment is to obtain an overview of sediment quality on a cantonal or regional scale, a succinct and not too complex study may be sufficient. If the aim is, however, to prioritize and focus future management activities to achieve management goals (e.g. source identification and control, remediation) or to assess potential biological impacts at identified hot spots, it may be necessary to characterize site conditions more comprehensively. The types of tools and information required for assessment is ultimately a choice made by the environmental manager and should be selected on a case-by-case basis. The following sections provide a brief discussion on various assessment tools that may be used when assessing sediment quality.

6.1. Tier 1: Assessment based on SQC comparison to measured concentrations

The first tier consists of chemical analyses and quantification of the substances of interest. These measurements are done on the < 2 mm fraction to exclude coarse material and debris with low capacity for binding contaminants. Concentrations below the SQC indicate which chemicals and sites are of little ecotoxicological concern. Further investigations at these sites would be of low priority and management options (if any) would focus on the protection of existing sediment quality conditions. Further assessments may be required, for example, for chemicals that are detected in the sediment and where SQC are not available.

If the matrix for analysis is the 2 mm fraction, the ecotoxicological risk can be estimated by comparing environmental concentrations of the target substances measured in sediment samples with the corresponding SQC derived for this purpose (Table 10). SQC derivation is largely based on

the EU Technical Guidance for Deriving Environmental Quality Standards (TGD), published by the European Commission in 2011 and updated in 2018 (EC 2018; Annex 3). SQC are derived using ecotoxicological effect data and represent threshold concentrations for risk in benthic organisms above which adverse effects cannot be ruled out. For most substances, the protection objective is preventing benthic communities from deterioration. For some substances that tend to bioaccumulate and biomagnify (e.g. PCBs, PFOS), the protection objective of secondary poisoning in organisms higher in the food chain (e.g. fish, birds, mammals)[20] has been taken into consideration in the SQC derivation process. Substance dossiers with SQC derivation described in detail are available upon request at the Ecotox Center (info@oekotoxzentrum.ch). The Ecotox Center has also derived *Ad Hoc* SQC for other substances as needed. These Ad Hoc SQC are not externally reviewed but are also available upon request.

The Risk Quotient (RQ) is derived using the following formula:

$$Risk\ Quotient\ (RQ) = \frac{Measured\ Environmental\ Concentration\ (MEC)}{SQC}$$

In general, when SQC are exceeded, it cannot be ruled out that contamination poses a threat to aquatic life (EC 2018). The risk for benthic organisms is considered tolerable if the RQ <1 and non-tolerable when the RQ ≥1.

In general, for organic compounds SQC are derived for sediment with 1% TOC as a worst case.

Where indicated (Table 10), measured environmental concentrations should be normalized to the TOC content in sediment before comparison with the corresponding SQC as follows[21]:

$$MEC_{norm} = \frac{MEC}{f_{TOC}}$$

Where:

MEC_{norm} = measured environmental concentration normalized to 1% TOC

MEC = non-normalized measured environmental concentration

f_{TOC} = fraction of total organic carbon in the sediment being assessed in %

Normalization is recommended for TOC content between 1 and 10 %. This normalization approach is a simplification which assumes a linear relationship between the concentration of TOC and bioavailability, which determines toxicity. Outside of the 1-10% TOC range, there is some uncertainty associated with normalization which must be taken into account in the assessment.

[20] Human health was outside the scope of this project but should be considered (e.g. intake of contaminants via ingestion) if actions such as remediation or dredging are the objective of a study.

[21] It is also possible to normalize the SQC to the TOC in the sediment at issue as follows:

$$SQC_{norm} = SQC \times f_{TOC}$$

where SQC_{norm} is the SQC normalized to the TOC content in sediment, SQC is the SQC for 1 % OC and f_{TOC} is the fraction of total organic carbon in the sediment at issue in %.

Table 10: Sediment quality criteria (SQC) proposed for the substances selected for sediment monitoring in Switzerland. P: preliminary values, which should not be used for determining quality classes due to high uncertainty.

Substance	CAS	Units	SQC [a, b]
Cu	7440-50-8	mg/kg d.w.	9.9 [c]
Zn	7440-66-6	mg/kg d.w.	99.7 [d]
Hg	7439-97-6	mg/kg d.w.	0.102 [d]
Pb	7439-92-1	mg/kg d.w.	50.3
PAH (16 indicator)	NA	--	--
Naphthalene	*91-20-3*	*µg/kg d.w.*	*30.2 (P)* [c]
Acenaphthylene	*208-96-8*	*µg/kg d.w.*	*30.5 (P)* [c]
Acenaphthene	83-32-9	µg/kg d.w.	97.0 [c]
Fluorene	*86-73-7*	*µg/kg d.w.*	*142.4 (P)* [c]
Phenanthrene	85-01-8	µg/kg d.w.	78.0 [c]
Anthracene	120-12-7	µg/kg d.w.	4.7 [c]
Pyrene	129-00-0	µg/kg d.w.	167.0 [c]
Fluoranthene	205-99-2	µg/kg d.w.	410.0 [c]
Chrysene	*218-01-9*	*µg/kg d.w.*	*279 (P)* [c]
Benz[a]anthracene	*56-55-3*	*µg/kg d.w.*	*60.2 (P)* [c]
Benzo[k]fluoranthene	*207-08-9*	*µg/kg d.w.*	*135.1 (P)* [c]
Benzo[b]fluoranthene	*205-99-2*	*µg/kg d.w.*	*139.5 (P)* [c]
Benzo[a]pyrene	*50-32-8*	*µg/kg d.w.*	*183 (P)* [c]
Benzo[ghi]perylene	*191-24-2*	*µg/kg d.w.*	*83.9 (P)* [c]
Dibenz[a,h]anthracene	*53-70-3*	*µg/kg d.w.*	*27.3 (P)* [c]
Indeno[1,2,3-cd]pyrene	*193-39-5*	*µg/kg d.w.*	*63.9 (P)* [c]
PCBs (7 indicator)	NA	--	--
PCB 101	*37680-73-2*	µg/kg d.w.	*0.108 (P)* [c]
PCB 118	*31508-00-6*	µg/kg d.w.	*0.25 (sec.pois.)(P)* [c, f] *0.05 (sec.pois.)(P)* [c ,e ,f]
PCB 138	*35065-28-2*	µg/kg d.w.	*0.2 (P)* [c]
PCB 153	*35065-27-1*	µg/kg d.w.	*0.3 (P)* [c]
PCB 180	*35065-29-3*	µg/kg d.w.	*0.088 (P)* [c]
PCB 28	*7012-37-5*	µg/kg d.w.	*0.008 (P)* [c]
PCB 52	*35693-99-3*	µg/kg d.w.	*0.02 (P)* [c]
PBDEs (sum 6 indicator 28, 47, 99, 100, 153, 154)	NA	µg/kg d.w.	*52.0* [c] *0.90 (sec.pois.)* [f]
Nonylphenols	NA	µg/kg d.w.	131 [c]
Octylphenols	NA	µg/kg d.w.	12.1 [c]
DEHP	117-81-7	mg/kg d.w.	1.08 [c]

Substance	CAS	Units	SQC [a, b]
Diuron	*330-54-1*	*µg/kg d.w.*	*0.39 (P)* [c]
Chlorpyrifos	*2921-88-2*	*µg/kg d.w.*	*0.03 (P)* [c]
Cypermethrin	*52315-07-8* [a]	*µg/kg d.w.*	*0.018 (P)* [c]
Tebuconazole	107534-96-3	µg/kg d.w.	2.8 [c]
Ciprofloxacin	*85721-33-1*	*µg/kg d.w.*	*402 (P)*
E2-E1-EE2	*50-28-2* *53-16-7* *57-63-6*	*µg/kg p.s.*	*E1: 0.018 (P)* *E2: 0.008 (P)* *EE2: 0.001 (P)*
Triclosan	*3380-34-5*		*67.4 (P)* [c]
PFOS	*1763-23-1*	*µg/kg d.w.*	*2.7 (P)* [c] *1.85 (sec.pois.)* [f]
Tonalide	21145-77-7	µg/kg d.w.	344 [c]
HCBD	*87-68-3*		*2.4 (P)* [c, f]

[a] The SQC values may change if more effect data becomes available. The Ecotox Centre will publish the most up to date values at: www.ecotoxcentre.ch

[b] SQC are classified as preliminary (P) if not enough effect data are available for their derivation (see Annex 3). See text on how they can be used for the assessment.

[c] Derived for 1 % TOC. Normalisation for the TOC content recommended.

[d] Added Risk Approach. The SQC can be adapted to the local situation by adding to the background concentration 17.9 mg/kg for Zn and 0.016 mg/kg d.w. for Hg.

[e] Protects from all planar PCBs.

[f] Substance potentially bioaccumulated and biomagnified. The SQC is intended to protect top predators from secondary poisoning.

6.1.1. Classification in quality classes

The evaluation system proposed for assessing sediment quality based on SQC uses five categories or classes based on the RQ (Table 11).

When the measured concentration in sediments is lower than the SQC, (RQ<1) the sediment quality is *very good* or *good*. When the measured concentration in sediments is higher than the SQC, (RQ≥1) the sediment quality is *moderate*, *unsatisfactory* or *poor*.

The implementation of this classification system is only possible for substances with definitive SQC values. For the assessment of substances with a preliminary SQC, marked with a (P) in Table 10, classification into sediment quality classes should not be performed because the SQC values entail high uncertainty. SQC are classified as preliminary if the assessment factor for SQC derivation was higher than 50 or the SQC is derived using the equilibrium partitioning approach (Annex 3). The color code to be attributed in such cases is *grey*, for *not assessable*.

Preliminary SQC are complemented with additional effect concentrations for benthic organisms (Annex 4). These effect concentrations can be used to refine the assessment performed through SQC comparison when available[22].

Table 11: Sediment quality assessment system based on SQC comparison.

Classification		Numerical evaluation		Class definition (RQ = MEC/SQC)	Meaning
	Very good	0.8 – 1	The measured concentration in the sediment is at least 10 times lower than the quality criterion (SQC)	RQ < 0.1	SQC met
	Good	0.6 - <0.8	The measured concentration in the sediment is between 1 and 10 times lower than the quality criterion (SQC)	0.1 ≤ RQ < 1	
	Moderate	0.4 - <0.6	The measured concentration in the sediment is lower than two times the quality criterion (SQC)	1 ≤ RQ < 2	SQC exceeded
	Unsatisfactory	0.2 - <0.4	The measured concentration in the sediment is lower than 10 times the quality criterion (SQC)	2 ≤ RQ < 10	
	Poor	0 - <0.2	The measured concentration is equal to or higher than 10 times the quality criterion (SQC)	RQ ≥ 10	

In addition to the classification, a numerical score between 0 and 1 can be specified according to the approach followed in other modules of the modular stepwise procedure. In this approach the class limit between moderate and good corresponds to 0.6 and the other class limits are interpolated linearly (Table 11 and Figure 10).

[22] When preliminary SQC are determined by the equilibrium partitioning approach (EqP), reliable effect concentrations for benthic organisms are not available.

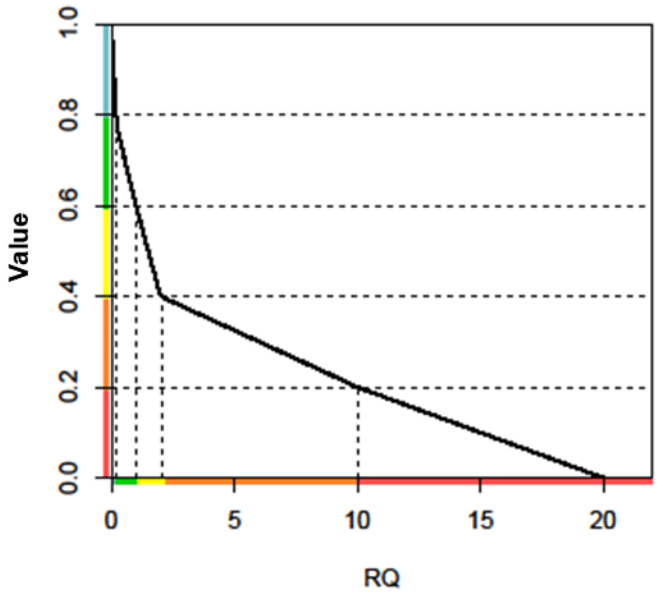

Figure 10: Value function to convert the risk quotient into a standardized assessment between 0 and 1 according to the modular stepwise procedure.

Dealing with concentrations below the limit of detection or quantification

If the measured concentration (MEC) is below the limit of detection (LOD) or quantification (LOQ) of the analytical method, we can distinguish different situations:

- SQC > LOQ

If the MEC is lower than the LOQ (or LOD) but the SQC is higher than the LOQ, then the SQC is met and the quality of the sediment is considered *good or very good*. If the SQC is definitive and at least ten times higher than the LOQ (or LOD), the quality of the sediment is considered *very good*.

- SQC < LOQ[23]

If the SQC is lower than the LOQ but higher than the LOD and if the MEC is lower than the LOD, then the SQC is met and the quality of the sediment is *good*. The result of the analysis is indicated as < x (units), where x is the LOD.

If the MEC is lower than the LOQ but higher than the LOD, then it is not possible to assess the quality of the sediment and determine the quality category. The color attributed is *grey*, which corresponds to a *non-assessable* quality, and the result of the measurement is indicated as < x (units), where x is the LOQ.

[23] It is advisable to contact the laboratory in charge of chemical analyses during the study design to ensure that the analytical techniques are suitable for the objectives (comparison with the SQC). If possible, each laboratory should improve analytical methods to achieve the level of SQC.

- SQC < LOD

If the MEC is lower than the LOD, then it is not possible to assess the quality of the sediment and determine a quality category. The color is *grey*, which corresponds to a *non-assessable* quality, and the result of the measurement is indicated as < x (units), where x is the LOD.

6.1.2. Alternative methods for evaluating sediment quality based on the fine fraction

It is not possible to derive SQC for the fine fraction (< 63 µm) because effect concentrations from spiked sediment toxicity tests used in the derivation process are generally expressed for total sediment (< 2 mm). When the fine fraction is the matrix chosen for the chemical analyses, the Target Values (TV) proposed by LAWA (1998) are recommended (Table 12; AWEL 2018). These TV were derived specifically for suspended matter/sediment but are not based on ecotoxicological data, therefore they are not necessarily protective for benthic organisms. The assessment conclusions are either *achieved* or *not achieved*.

Table 12: Assessment of sediment contamination according to the LAWA-Target Values for suspended matter / sediments (LAWA 1998). All concentrations in dry weight.

Substance	Units	Target Value
Cd	mg/kg	1.5
Cr	mg/kg	100
Cu	mg/kg	60
Hg	mg/kg	1
Ni	mg/kg	50
Pb	mg/kg	100
Zn	mg/kg	200
Benzo(a)pyrene	mg/kg	0.4
Hexachlorobenzene	µg/kg	40
PCB 153	µg/kg	4
Σ_7 PCBi	µg/kg	28

6.1.3. Mixture risk assessment

The assessment and classification system presented in 6.1.1 is based on measured concentrations of individual substances, but sediment contamination most commonly occurs as mixtures. As part of Tier 1, it may be relevant to assess mixture toxicity (Figure 9). Current knowledge in the area of mixture toxicity indicates that the risk/toxicity of a mixture of chemicals is mostly additive and therefore higher than that of any of the individual components of the mixture individually (Kortenkamp et al. 2009). The concentration addition, which consists of summing the RQ for the individual components of the mixture[24], is thought to be applicable to mixtures of chemicals with

[24] The most common approach used in sediment risk assessment for mixture toxicity is the mean-PECQ. The mean-PECQ is essentially an additive model that uses empirical sediment benchmarks (Predicted Effect Concentrations –PECs) as weighting factors for contaminants or contaminant classes within the mixture (MacDonald and Ingersoll 2000). Instead of the sum, the mean-PECQ approach adds average scores calculated individually for major contaminant classes, i.e. metals, PAHs, PCBs and organochlorine pesticides. Based on field validation, a sediment sample is considered toxic to benthic invertebrates if the mean-PECQ≥0.5 (Ingersoll et al. 2001). Such validation with field data has not been performed neither for the mean quotients calculated using the SQC nor for the RQ_{mix}.

a similar mode of action. For chemicals with different mechanisms of action it appears to be slightly conservative (protective), showing a relatively small likelihood of underestimating effect. Therefore, it can be used for screening-level evaluations in Tier 1 as follows:

$$RQ_{mix}=\sum_{i=1}^{n}\frac{MECi}{SQCi}$$

6.2. Tier 2: Risk assessment refinement

The potential hazard identified in Tier 1 through exceedance of the SQC should be confirmed through a more detailed, site-specific, risk assessment if management strategies are foreseen (Tier 2). Additional assessments should be selected on a case-by-case basis so as to define the occurrence, nature, and severity of adverse biological effects associated with sediment-bound contaminants. A refinement of exposure assessment (Chapter 6.2.1) can be performed by taking into consideration background levels of contamination at the site or using chemical proxies for bioavailability[25]. Indeed, transformation processes, complexation and ageing of substances bound to sediments can lead to profound changes in their bioavailability. Furthermore, biological tests (Chapter 6.2.2) can be used in conjunction with chemical analyses of sediments as a direct measure of toxicity of sediment-bound chemicals, taking into account mixture toxicity of measured and unmeasured chemicals. *In situ* community studies provide information on direct and indirect effects at higher levels of organization. The publications from Beauvais et al. (2020) and Casado-Martinez et al. (2021) provide information on the implementation of the two-tier assessment.

6.2.1. Refinement of exposure assessment

Natural background concentrations

The presence of naturally occurring chemicals (i.e. metals and certain organic compounds such as PAHs) results in natural background concentrations in all environmental compartments, including sediments with implications for quality assessment. Although it is possible that natural levels of chemicals contribute to adverse effects on certain aquatic organisms, managers may want to focus on sites and chemicals primarily influenced by human activities.

Natural background concentrations in Swiss sediments were taken into account - where possible - for the derivation of the proposed SQC. However, background concentrations may vary across regions in Switzerland (Casado-Martinez et al. 2016). If a substance naturally present in the environment exceeds its corresponding SQC, the evaluation can be refined using site-specific information on natural background concentrations to ensure that the SQC exceedance is not due to the site-specific natural background. However, there are no official values of background concentrations established for Switzerland. A review of the existing information for metals is available

[25] According to UN-GHS 2019 (UN 2019), bioavailability or biological availability is the extent to which a substance is taken up by an organism and distributed to an area within the organism. It is dependent upon physico-chemical properties of the substance, the anatomy and physiology of the organism, pharmacokinetics, and route of exposure.

(Casado-Martinez et al. 2016, Annex 5). Alternatively, background concentrations can be estimated from data obtained from reference sediments far from any contaminant point sources and discharges. Reference sediments should be of comparable grain size. If sufficient data is available, background concentrations may also be derived statistically from distributions of measured concentrations (EC 2018).

Human activities are the only source of synthetic organic contaminants to the environment; therefore, natural background concentrations of such compounds should be zero. However, some substances, such as PCBs, may be ubiquitous and present even at sites far from sources due to their persistence and long-range atmospheric transport. For such substances, it may be relevant to use ambient or baseline background concentrations[26] at sites far from point sources and discharges (e.g. concentrations of PCBs in pristine alpine lakes) to set realistic management objectives.

Chemical proxies for bioavailability

- Metals

It is recommended to explore the relative importance of sediment properties driving metal bioavailability. Estimating the metal not bound to sulfides may be a good approach for divalent metals (Hg, Cu, Pb, Zn, Ni) as it provides an estimate of the potential bioavailable fraction in the sediment interstitial water (SEM-AVS theory, MERAG 2016). It should be noted that natural sediment in lowland rivers commonly contains a certain amount of sulfides, but nearly oxidized sediments and sediments from erosional environments generally have low concentrations. Other metals may bind to organic carbon (e.g. Cu) or iron/manganese oxides (e.g. Ni). An additional refinement tool is to use existing bioavailability models (e.g. the biotic ligand model, MERAG 2016) for predicting metal toxicity but such models have not been fully validated for sediment (Campana et al. 2013; Vangheluwe et al. 2013). A relatively simple estimation of metal bioavailability is to consider the proportion of the mineralized forms of metals in sediments. Mineralized metals are considered not bioavailable because they do not dissolve easily (in water or during the passage through the organism gut). Mineralized forms are estimated from the quantification of metals after cold extraction of sediments with a dilute acid (e.g. 30 min 1 M HCl (Simpson et al. 2013)), similar to that used for estimating the portion of metals not bound to sulfides. However, metal concentrations determined after dilute acid extraction are not recommended in Tier 1 because some forms of metals, such as Cu or Hg, are not extracted with this technique.

[26] According to ECHA (2008):

- Natural background concentration: the natural concentration in the environment that reflects the situation before any human activity disturbed the natural equilibrium. As a result of historical and current anthropogenic input from diffuse sources, the direct measurement of natural background concentrations is challenging;
- Ambient background concentration: the sum of the natural background of an element with diffuse anthropogenic input in the past or present (i.e., influence of point sources not included);
- Baseline background concentration: the concentration in the present or past corresponding to very low anthropogenic pressure (i.e., close to the natural background).

- Organic contaminants

For organic contaminants that bind preferentially to organic matter, Tier 1 initially foresees normalization to the total organic carbon concentration of the sediment for comparison with SQC, which are derived for a sediment with 1% organic carbon as a worst case. While this normalization has proven suitable to account for differences in bioavailability at low and high ranges of organic carbon content, uncertainty remains as regards the linearity of the relationship between bioavailability and organic carbon content in the intermediate range. Further refinements may consider not only the quantity but also the quality of organic carbon (e.g. black carbon, humic acids, sawdust; Sinche et al. 2018). Partial/ mild extraction-based approaches also show good potential for the refinement of sediment risk assessments (e.g. Lydy et al. 2018, Yang et al. 2016). The most appropriate method will depend on the type of matrix and the chemical (Cui et al. 2013).

Passive sampling methods

Because dissolved concentrations in porewater may be a relevant exposure metric for risk assessments, the use of passive sampling methods[27] has received increasing interest as they provide a simpler, less disruptive sampling approach than conventional methods for collecting porewater. They have been used mainly for PCBs, PAHs and other legacy contaminants such as organochlorine pesticides. For a detailed review of passive sampler use in sediment assessment, it is recommended to consult Peijenburg et al. 2014 (metals) and Lydy et al. 2014 and Ghosh et al. 2014 (organics). Greenberg et al. (2014) provide detailed information on how passive sampling methods can be used to better inform decision-making in the process of assessing and managing contaminated sediment sites. Zennegg et al. (2016b) provide recommendations for the use of passive samplers (and sediment analysis) for PCBs.

6.2.2. Refinement of effect assessment

Bioassays

- Sediment contact tests

The most relevant matrix to test is the freshly collected whole sediment as this is closest to conditions in the field. Standard protocols from the International Organization for Standardization Water Quality series are available for sub-chronic tests with crustacean ostracods (*Heterocypris incongruens*, ISO 14371:2012) and nematodes (*Caenorhabditis elegans*, ISO 10872:2010) as well as for a chronic test with amphipods (*Hyalella azteca*, ISO 16303:2013) and a test with rooted macrophytes (*Myriophyllum aquaticum*, ISO 16191:2013). Other national and international agencies have standardized sediment toxicity tests that are suitable for evaluating the toxicity of environmental sediment samples for midges (*Chironomus* sp., OECD 2018:2004 and OECD 233:2010), oligochaetes (*Lumbriculus variegatus* OECD 225:2007) and amphibians (ASTM

[27] According to Parkerton and Maruya (2014): “Passive sampling methods can be broadly defined as techniques that rely on the partitioning of contaminants from the sampled media (e.g., sediment) to a reference sampler phase, typically a polymer, to concentrate the analyte of interest.”

E2591:2013). Whereas sufficient information may occasionally be gained using acute bioassays (e.g. for high levels of contamination), longer exposures or quantification of more specific effects at the sublethal level may be needed where moderate contamination levels or specific types of pollutants are present (chronic bioassays). Chronic tests are particularly relevant for benthic invertebrates, which can be exposed to low levels of pollution for extended periods. Although there is evidence on the sensitivity of some test species to certain types of chemicals (e.g. crustaceans and insects are most sensitive to insecticides), there are no recommendations on the most appropriate toxicity tests for particular types of contamination. The use of a battery of several bioassays with different test organisms and exposure routes, different test endpoints and exposure durations is therefore recommended to cover a range of effects and sensitivities exhibited by benthic organisms (e.g. Casado-Martinez et al. 2019).

- Alternative and emerging toxicity testing

In addition to whole sediment toxicity tests, bioassays may be performed on suspended sediments, elutriates, sediment extracts or porewater. Suspended sediments and elutriates are routinely used to measure the toxicity of contaminants released from sediments to the water column during disposal of dredged material or during sediment resuspension events, offering unique information compared to whole sediment tests (Haring et al. 2010). The testing of organic extracts involves the extraction and manipulation of sediments with solvents to obtain a suitable sample for testing and are relevant for testing the toxicity of the organic chemicals bound to the sediments. They are particularly suited for testing specific modes of toxic action *in vitro* such as estrogenicity, genotoxicity, cytotoxicity, etc. The standardization of such methods for testing surface water will facilitate their application to more complex matrices such as sediments, which is still in the development stage (Kizgin 2019; Li et al. 2013; Müller et al. 2019).

Recurring difficulties persist in integrating and comparing results from laboratory-based toxicity tests with field observations. To address this problem, *in situ* bioassays consisting of caged individuals (organisms reared in the laboratory or transplanted from a reference site) exposed to sediments on site can be used. This approach limits artefacts due to sampling, transport, and storage of sediment samples intended for laboratory toxicity tests and appears suitable for in-depth site-specific studies, e.g. for monitoring impacts of known discharges or remediation success (Ferrari et al. 2014, 2019). Although integration of complex site-specific conditions represents a strength for *in situ* methods, it can also increase the difficulties in interpreting responses of organisms obtained with such bioassays. An ongoing challenge is to develop robust *in situ* methods that allow accurate measurements of biological responses to varying environmental conditions.

Benthic community studies

The study of the composition of *in situ* benthic communities complements the information provided by bioassays and chemical analyses. While toxicity tests and chemical analyses can indicate the

likelihood of negative effects from contaminated sediments, the study of resident benthic communities allows an assessment of the effect of pollutants in the natural environment on a large number of species.

A number of indices based on the study of the structure of benthic macroinvertebrate communities are used in Switzerland to assess water quality (Burdon et al. 2019). The IBCH quality index is well established and is included in the Modular Stepwise Procedure (OFEV 2019). It allows the biological quality of rivers to be assessed on the basis of their colonization by invertebrate fauna such as insect larvae, small crustaceans, gastropods, mussels and worms. This index makes it possible to show deficits, particularly in terms of water quality and the structural diversity of habitats. In general, degradation of the aquatic environment can be diagnosed if sensitive organisms such as amphipods and EPTs (mayflies, plecoptera and trichoptera) are absent from the community - especially for hard substrates - and if it is dominated by pollution tolerant taxa such as certain worms (in particular tubificids) and chironomid larvae (Lang 2010). An evaluation of the quality of fine / sandy sediments requires the application of indices specifically developed for this type of substrate, such as the Oligochaetes Index of Sediment Bioindication (IOBS) and the Oligochaetes Index of Lake Bioindication (IOBL, % of individuals belonging to sensitive species / taxa), both standardized by the French Standardization Agency (AFNOR 2016), and the SPEAR nematodes index (NemaSPEAR; Höss et al. 2017). Oligochaetes are widely used in Switzerland to assess the quality of fine / sandy sediments of lakes (e.g. Lods-Crozet and Reymond 2005, Vivien and Ferrari 2019) and streams (e.g. Vivien et al. 2020a). The application of these indices, based on the reduction in the percentage of individuals belonging to sensitive to moderately sensitive species in the event of contamination of the sediments, requires a high level of expertise in systematics, which prevents their widespread use for routine analyses. However, the use of these indices will soon be facilitated by the use of genetic approaches for species identification (Vivien et al, 2020b).

Bioaccumulation studies

For chemicals known to bioaccumulate and biomagnify along the food chain such as PCBs and PFOS, exceedance of SQC should trigger site-specific studies of the levels of chemicals in aquatic biota. Such information provides a basis for determining the significance of chemical levels in sediments relative to the protection of the health of (wildlife) consumers of aquatic organisms. Bioaccumulation may be assessed directly in field-collected organisms by using caged individuals or in the laboratory under controlled exposure conditions, or using predictive bioaccumulation and food web models. Benthic macroinvertebrates are relatively sedentary and can consequently be exposed to sediments throughout all or most of their life cycle. They are abundant, easy to collect, and are ubiquitous across a broad array of sediment types. When it is not possible to directly assess bioaccumulation in field organisms, bioaccumulation studies can be performed in which organisms are exposed to field-collected sediments under controlled exposure conditions in the laboratory (e.g. using the standard bioaccumulation test with benthic oligochaetes, OECD

315:2008) or deployed for a sufficient period of time at the study site to account for environmental conditions (Alric et al. 2019).

- Biota standards

For substances posing a significant risk through indirect toxicity (secondary poisoning resulting from food-chain transfer) or when the analysis is more feasible in other environmental matrices, a biota standard may be derived (EC 2011, 2018). Biota standards can be derived either to protect humans from adverse effects resulting from the consumption of chemical-contaminated fishery food or to protect wildlife (predators, birds, and mammals) from risks of secondary poisoning brought about by consuming toxic chemicals in their prey. Biota standards should protect both benthic and pelagic predators (e.g. predatory fish) that may be at risk from secondary poisoning. However, toxicity studies reporting deleterious effects of dietary and oral exposure in aquatic predators are scarce. Biota standards based on birds and mammals assume that these values provide adequate protection to other taxa that might be at risk from secondary poisoning. They are expressed as chemical concentrations in the critical food organism of predators (prey fish, molluscs, crustaceans or other biota chosen according to the bioaccumulation characteristics of the substance) and assessment is based on direct measurements of field-collected organisms. WFD quality standards for biota are available for hexachlorobenzene, hexachlorobutadiene and mercury and its compounds (Daughter Directive to the WFD on EQSs (2008/105/EC)) as well as for brominated diphenylethers, fluoranthene, benz[a]pyrene and associated PAHs, dicofol, PFOS, dioxins and dioxin-like compounds, hexachlorocyclododecane and heptachlor(epoxide) (Directive 2013/39/EC).

7. Conclusions and perspectives

Different sampling and assessment strategies are used all over Switzerland. This is a real impediment to obtaining a global vision of the quality of the sediments and to applying the same criteria for decision-making (e.g. need for remediation or control measures) at the national level. Here, the proposed assessment strategy intends to harmonize sampling strategies and quality assessment, supporting uniform practice for sediment monitoring by cantonal authorities. It is based on a tiered framework in which Tier 1 involves risk assessment by comparing with SQC while Tier 2 involves more detailed assessments in the case of exceedance. It builds on practices already used at the national level in order to ensure as much as possible temporal continuity in existing databases and in the standard protocols and recommendations proposed at the international level for harmonization with current European practices.

It is not possible to recommend a single methodology suitable for all study objectives considering the great variety of objectives and types of water bodies present in Switzerland. Therefore, recommendations are provided to choose the most appropriate one, depending on the objective pursued and the characteristics of the sedimentary matrix of the study site. It is important that the results of the studies be accompanied with information on the analyzed matrix (< 2 mm or < 63 µm) and its properties (grain size and organic matter) so that sound information on the bioavailability of sediment-bound contaminants is available. Overall, this will allow greater knowledge of sediment quality in Switzerland to be acquired in the coming years.

The list of substances proposed for sediment monitoring relied heavily on previous prioritization exercises and substance properties given the limited data on measured environmental concentrations for Swiss sediments. The list of substances should be reviewed and, if necessary, updated based on the data acquired in the monitoring campaigns and regulations pertaining to chemical substances. In sediments, both current-use substances as well as compounds regulated or banned may be contaminants of concern depending on their environmental persistence. Thus, data acquisition campaigns may still be needed for chemicals that have been recently regulated until concentrations decrease to levels of low concern.

The proposed sediment quality criteria (SQC) reflect current scientific knowledge of effects on aquatic organisms. For some of these chemicals there is still little information on their ecotoxicology and the criteria are conservative so as to take into account the remaining uncertainty. These values should be updated in the future as new scientific evidence arises. Priority should be given to refining criteria with high remaining uncertainty when monitoring campaigns exhibit high incidence of exceedance.

Mixture toxicity is even more relevant for sediments than for surface waters because of long-term storage of (persistent) substances in this environmental compartment. Here the sum of the risk quotients (RQ) approach proposed for surface water assessment is suggested for bed sediments in order to assess substances with similar mode of toxic action. Nevertheless, this approach should be subject to validation before extended use.

When comparison with the proposed environmental quality criteria (SQC) induces a non-satisfactory quality of the sediment evaluated, a risk assessment refinement is proposed (Tier 2). However, the different tools that can be used in such cases still need validation with respect to water bodies and pollution sources relevant to Switzerland. This means, for instance, testing the sensitivity and the robustness of bioassays with regard to specific types of pollutants as well as developing appropriate interpretative guidance.

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Glossary

AF:	*Assessment Factor:* In the process of deriving SQC and EQS, the adjustment factor used to extrapolate the relationships (dose-response) observed experimentally in order to estimate the concentration (SQC or EQS) below which no deleterious effect is likely to occur.
Benthic:	Refers to organisms living on or in the sediment of aquatic habitats.
Bioaccumulation:	The process by which chemicals accumulate in aquatic organisms either directly from water or by ingestion of food containing these substances.
Bioassay:	Test used to assess the relative toxicity of a substance or sample by measuring its effects on a living organism compared to a control.
Bioavailability:	*Capable of being absorbed by organisms.*
Biomagnitication:	Result of the bioaccumulation process by which the concentrations of compounds accumulated in the tissues increase from one trophic level to another, moving higher up in the food chain. This term implies an efficient transfer of chemicals from the food to the consumer so that the residual concentrations increase systematically from one trophic level to another.
BSAF:	*Biota Sediment Accumulation Factor:* ratio between the concentration of a hydrophobic organic substance in the organism, adjusted according to the lipid content, and the concentration of this compound in the sediment to which the organism is exposed, adjusted to the level of organic carbon. *Source:* https://bsaf.el.erdc.dren.mil/about.cfm.
Background concentration:	Part of ambient contamination levels that cannot be attributed to emissions in the study area.
Composite sample:	A sample composed of two or more sub-samples, mixed in suitable proportions in a discrete or continuous manner, for which it is desired to obtain the mean value of a given characteristic. *Source:* ISO 5667-12: 1995.
DEHP:	*Bis(2-ethylhexyl) phthalate*.
Diffuse pollution:	Pollution due to dispersed activities without a punctual source of emission.
E1:	*Estrone*.
E2:	*17β-estradiol*.
EE2:	*17α-ethinylestradiol*.
EqP:	*Equilibrium partitioning:* mechanistic approach used to derive environmental quality standards for sediments. It assumes that the toxicity of a nonionic organic compound in the sediment is proportional to its concentration in water. The concentration of this potentially toxic compound in the sediment can then be estimated if the relationship between the concentrations in the porewater and in the sediment is known.
EQS:	*Environmental quality standard.*

Fine sediment:	Here, this term is used for sediments with a grain size < 63 µm.
FOEN:	*Federal Office of the Environment.*
f_{TOC} *:*	Mass fraction of organic carbon in sediments. Expressed in kg/kg.
HCBD:	*Hexachlorobutadiene*.
ICPR:	*International Commission for the Protection of the Rhine.*
LC/EC50 :	Effect concentration causing 50% mortality or acute effect.
LOD:	*Limit of detection:* signal or output concentration above which it can be said with a defined level of confidence that a sample is different from a control not containing the desired compound. *Source:* EC 2010.
LOQ:	*Limit of quantification:* a defined multiple of the detection limit set at a concentration of the target compound which can be reasonably determined with an acceptable level of accuracy and precision. The LOQ can be calculated using a reference compound or sample by considering the lowest calibration point on the calibration curve excluding the control. *Source:* EC 2010.
Matrix:	*Mass of particles of small particle size.*
MEC:	*Measured environmental concentration.*
MSP:	*Modular stepwise procedure.*
NOEC:	*No Observed Effect Concentration*.
OCS:	*Ordinance on Contaminated Sites.*
PAHs:	*Polycyclic aromatic hydrocarbons.*
PBDEs:	*Polybrominated diphenyl ethers.*
PCBs:	*Polychlorinated biphenyls*.
PCDD/F:	*Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans.*
PEC:	*Probable Effect Concentration:* contaminant concentration likely to produce an effect in benthic invertebrates (MacDonald et al. 2000). Concentrations above the corresponding PEC value pose a probable risk to benthic communities. See Box 1.
PFOS:	*Perfluorooctanesulfonic acid.*
Point source:	Site or fixed installation from which pollutants are emitted; any separately identifiable source of pollution; a pipeline, for example.
$QS_{hum.cons.}$*:*	Quality standard derived to protect humans from secondary poisoning *(see Box 1).*
RQ:	*Risk quotient:* calculated as $RQ = \frac{MEC}{SQC}$

Sediment:	Unconsolidated mineral and organic particulate material deposited at the bottom of aquatic environments.
SMP:	*Sediment management plan* from the International Commission for the Protection of the Rhine.
Stormwater overflow:	Unit sewerage networks, designed to collect rainwater and domestic effluents in common pipelines, can be saturated during periods of heavy rainfall or snowmelt. They are equipped with stormwater overflows which allow excess flow to be diverted to the nearest river or to other bodies of water.
SQC:	*Sediment quality criteria*: See SQG.
SQG:	*Sediment quality guideline*: Contaminant concentration defined to protect the health of the sediment ecosystem or to predict negative effects on that ecosystem, or both.
Suspended matter:	Fine particles suspended in water. Some are naturally present in river water, such as plankton, plant debris and minerals, while others are of human origin (organic and inorganic matter).
SwissPRTR:	*Swiss Pollutant Release and Transfer Register.*
TEC:	*Threshold Effect Concentration:* (see Box 1).
TGD:	*Technical Guidance Document:* technical guide published by a government authority or body that sets out the recognized technical practices that are necessary to meet the regulatory requirements in force.
TMF:	*Trophic Magnification Factor:* calculated from the slope of the regression curve between the chemical concentration and the tropic level of organisms in the food web.
Total or whole sediment:	Here, sediments with grain size < 2 mm.
Uncertainty:	Estimate associated with the result of a test which characterizes the range of values in which the true value is found.
WFD:	*EU Water Framework Directive.*

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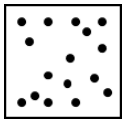
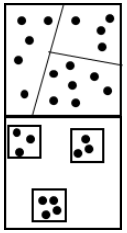
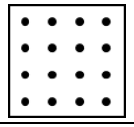
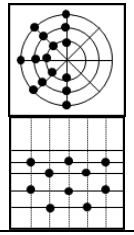
Annex 1: Types of sampling design

Table 13: Types of sediment sampling strategies.

Type	Execution	Advantages	Disadvantages	Consider using if	In order to
Simple random 	Samples are randomly located	- All sampling units have the same and known probability of being selected - Low systematic errors	- High number of samples required - Costly execution - Proportional distribution of sampling sites	- Estimating the prevalence of sediment contamination - Analytical costs are high compared to sampling costs	- Produce equally precise or more precise data with fewer analyses and lower costs
Stratified / multistage 	Large subareas are selected, then stations are randomly located within each subarea to yield average or pooled estimates of the variables of interest	- Flexible - Heterogeneity over time and space considered - Reduced number of analyses for a given level of precision - Coverage is maximized, concentrating budget and efforts where needed	- Previous knowledge of local conditions required - Only with well-defined zones of different sediment types or land uses - Possibility of encountering unsampleable sites randomly selected	- Estimating relative amount (mean) of a contaminant at a site location - Delineating the boundaries of an area of contamination - Under budget constraints - There exist spatial or temporal data	- Increase the precision of the estimate with equal number of samples, or achieve same level of precision with fewer samples and lower costs - For dredged material management programs, to represent specific areas
Systematic / in grid 	Samples are located at regular intervals after the first sampling location is chosen randomly	- Uniform location of sampling points - Homogeneous coverage of study area - Low costs if the study area is small	- Expensive unless the study area is small and/or the density of stations is relatively low - Wrong mesh size may introduce systematic errors	- To develop understanding of when contamination is present and adequate budget is available. - To produce information on spatial or temporal trends.	- To have an evenly distributed network of network of sampling points to enhance the probability of identifying hot spots

Targeted 	The distribution of sampling points is based on previous knowledge: e.g. point source	- Lowest sampling points as possible - Sampling is performed according to pollution sources and hypotheses	- High probability of systematic errors if hypotheses are wrong - Requires previous information e.g. preliminary survey	- To do an initial screening investigation on a relatively small-scale problem when having a limited budget and/or limited schedule	- To identify and monitor the impact at identified hot spots - Remediation planning and success control - Identifies need for statistical probabilistic sampling design

Annex 2A: Check list

Objectives / actions	Material	Complementary Information	Checked
Safety	Lifejacket	If depth < 1 m or > 50 cm with > 1 m/s	
	Portable phone		
	Gloves in latex, vinyl or nitrile	According to target analytes	
	First aid kit		
	Wheelies		
	Extra personnel		
Site characterization	Field sheet		
	GPS		
	Multiparametric device	pH, temperature, O_2, conductivity	
	Flowmeter	Flow measurement	
	Rub		
	Labelling material	Permanent markers, type, paper towels	
Sampling equipment	Scoop	Wadeable streams Stainless steel or plastic according to target analytes	
	Manual grab	Non-wadeable streams	
	Eckmann grab	By boat, bridge For metal analysis, sub-sample far from walls	
	Van Veen grab	By boat, bridge For metal analysis, sub-sample far from walls	
	Sediment core	When access by boat, bridge	
Collection Homogenization	Bucket 15 L Spatula	For metals	
	Bowl 15 L stainless steel Spatula stainless steel	For other target substances	
Analyses: Metals	Wide-neck vials (500 mL)	For cleaning : Table 6 Storage in plastic bags	
	2 mm sieve POM	$diameter_{min}$= 20 cm	
	Flat spatula in plastic		
	Small plastic scoop		

Objectives / actions	Material	Complementary Information	Checked
Analyses: Other substances Carbonates TOC – LOI	Wide-neck glass vials (500 mL)	For cleaning: Table 6 Storage in pre-treated aluminum foil	
	2 mm sieve in stainless steel	$diameter_{min}$= 20 cm	
	Spatula stainless steel		
	Bucket 15 L stainless steel		
	Small scoops		
Grain size	Small plastic bag	Can be sub-sampled from 500 mL sample	
Water content		Sample in the lab from 500 mL sample	
Transport	Cold box + cold blocks	2-8 °C, far from light	

Annex 2B: Field protocol [28]

1) Establish the necessary measures for the safety of operators (appropriate signalization when near a road, lifejacket, raw risk, etc.).

2) Complete the field sheet taking the necessary in situ values and drawing the site diagram.

3) Define the three cross-sections to be sampled and note the GPS coordinates. The principles to be respected in the choice of sections are:

- The sediment collected must be immersed throughout the year (also during low water).
- The sediment sampled should contain as large a fraction of fine particles as possible.
- The point where sediment is collected is located in a deposition zone, i.e. an area where the current is weak such as a concave zone and/or there is vegetation.

4) Take all necessary measures to avoid chemical contamination of equipment and samples.

5) Sampling is carried out in the downstream-upstream direction to avoid sediment remobilization.

6) Prepare all necessary equipment for sampling, sieving, homogenization and storage near the first cross section to be sampled (the section further downstream).

7) Test the depth, current and substrate nature of the cross-section before entering the river.

8) Take the first 2 to 10 centimeters of sediment in a non-contaminating (metal or plastic) bowl with the help of a (metal or plastic) scoop in at least three points per cross section to form a representative composite sample. At each sampling, empty the surface water contained in the scoop before collecting the sediment in the bowl.

9) If the sample is conclusive (e.g., sufficient fine sediment in the bowl), remove stones, leaves and other branches manually. Note any particularities of the sample in terms of color (change of color in contact with air), odor and consistency on the field sheet.

10) Homogenize the contents of the bowl until it has a uniform consistency, texture and color.

11) Sieve to 2 mm without adding water and collect the sieve in a second bowl.

12) Fill the pre-labelled wide-neck (glass or plastic) vial with the sieved sample to the brim. Before the vials are closed, a small amount of water from the site is added to the vial before it is closed to avoid contact of the sediment with the air.

13) Store the vials in a cooler away from light.

[28] This protocol should be used after reading the accompanying document Strategy for Sediment Quality Assessment.

Annex 2C : Field sheet

Field sheet – sediment sampling	
Name personnel:	Organisation:
Tel./ email :	Date and time:
Water body:	Coordinates: x: y:
Site:	Code:
Sampling objectives	
Site diagram Lenght of section: Width: *Specify flow direction, the location as well as the number of samples, please:*	

Activities in the surrounding area

☐ Natural

☐ Fields

☐ typy of culture: _____

☐ Leisure

☐ Industry

☐ type of industry: _____

☐ effluent

☐ Residential

☐ gardens

☐ stormwater overflow

☐ Discharge

☐ Agriculture

☐ Contaminated site

☐ Pasture

☐ Banks

☐ presence of cattle

☐ natural

☐ feeding area

☐ artificial

Meteorological conditions

Day of sampling	Previous day
☐ sunny	☐ sunny
☐ rain (1 light -> 3 heavy)	☐ rain (1 light -> 3 heavy)
☐ wind (1 faible -> 3 strong)	☐ wind (1 faible -> 3 strong)
☐ cloud cover (1 light -> 3 heavy)	☐ cloud cover (1 light -> 3 heavy)
☐ fog	☐ fog
☐ temperature (°C)	☐ temperature (°C)

In situ measurements

Conductivity (µS/cm):

Temperature (°C):

Dissolved oxygen (mg/L and %):

Rate of flow (m^3/s):

pH:

Other:

Type of sampling device:

Description of sediment sample

Color and intensity

(brown, grey, black, yellow, etc.)

Type of substrate

(sandy, silicious, fines, muddy)

Odour and intensity

(sulfur, chlore, benzene, ammonia, ferrous)

Living organisms

(crustaceans, insects, etc.)

Characterisation of samples				
Number / code	Location (x:y)	Depth / Volume	Description	Comments
Pre-treatment of samples				
Number / code	Nb. of sub-samples per composite	Homogenisation	Sieving	Comments

Transport and storage			
Number / code	Transport conditions	Storage conditions	Comments

Annex 3: SQC (EQS_{sed}) derivation method

The derivation of SQC is largely based on the EU Technical Guidance for Deriving Environmental Quality Standards (TGD), published by the European Commission in 2018 (EC 2018)[29]. The derivation process includes the following steps (Figure 10):

1. Search for acute toxicity data (LC/EC50), chronic toxicity data (NOEC) and field/mesocosm data. When sediment toxicity data are not available, water column toxicity data can be used (see step 3).
2. Data quality evaluation: the collected data are assessed for relevance and reliability.
3. SQC derivation: three different approaches are available depending on data availability:
    - Derivation using the "Species Sensitivity Distribution" (SSD) method. All the relevant and reliable toxicity data available on the different species are ranked and plotted (the lowest effect concentration per species and endpoint), and the hazardous concentration representing the concentration protective of 95% of all species (HC5) is calculated. This method can be applied when preferably more than 15, but at least 10 effect data from different species covering at least 8 taxonomic groups are available. To derive quality standards for protecting pelagic species, the following taxa would normally need to be represented (EC 2018): one fish species and a second family in the phylum Chordata, a crustacean species, an insect, a phylum other than Anthropoda or Chordata, an order of insect or any phylum not already represented, algae or cyanobacteria, and a higher plant. Guidance on the use of SSD for the derivation of sediment thresholds is currently not available; preliminary recommendations are provided in ECHA (2014). To account for residual uncertainty, the HC5 is divided by an AF. An AF of 5 is used by default but may be reduced based on the uncertainties associated with HC5 derivation (quality of the database, diversity and representativeness of the database, goodness of fit).
    - Derivation using the AF method. The lowest reliable and relevant effect datum is selected (preferably a NOEC or EC10 from a chronic test) and divided by an AF. The AF (Table 14) varies between 10 and 100 according to the number of data available on other species, representing different taxa and feeding behaviors (e.g. epibenthic grazers, sediment-ingesting worm, benthic filter-feeder). If only results from short-term tests with sediment-dwelling organisms are available, an assessment factor of 1000 is applied to the lowest reliable value. In such situations, a quality criterion should also be derived using the Equilibrium Partitioning approach and the lowest value would be proposed as the SQC.

[29] The 2018 document is an updated version of the EU TGD (EC 2011). The procedure for the derivation of EQS for protecting benthic organisms is largely the same.

Table 14: Assessment factors for the derivation of quality criteria for sediments (after EC 2018).

Available data	Assessment factor (AF)
Only short-term toxicity tests (LC50 or EC50)	1000
One long-term test (NOEC or EC10)	100
Two long-term tests (NOEC or EC10) with species representing different life histories and feeding behaviors	50
Three long-term tests (NOEC or EC10) with species representing different living and feeding conditions	10

- Derivation using the "Equilibrium Partitioning" (EqP) method and toxicity data from water column exposures. The EqP approach, which is based on the method developed by Di Toro et al. (1991) for deriving sediment quality guidelines, assumes that the toxicity of a non-ionic organic chemical in sediment is proportional to its concentration in pore water. The SQC can be calculated as follows:

$$SQC_{EqP} = QC_{fw,eco} \times K_{OC}$$

where $QC_{fw,eco}$ is the quality criterion or standard for surface waters based on long-term tests and K_{OC} is the partition coefficient of the chemical to sediment organic carbon. For this method, it is necessary to find the most precise partitioning coefficient for the chemical compound.

4. Comparison of the obtained values derived through the different methods with field or mesocosm data (if available).

Because of the relatively limited sediment toxicity database for some substances, the application of relatively high AF is required to account for residual uncertainties in the derivation of SQC. There is the possibility that the proposed SQC are too low, making compliance assessment difficult. For this reason, SQC are classified as definitive (D) or preliminary (P) according to the number of effect data used in their derivation: SQC are considered definitive if the AF applied is ≤ 50. If the AF applied is > 50 or the SQC is derived solely from water toxicity data through the EqP approach, SQC are considered provisional.

Effect data from tests where bioavailability is maximized are preferred because they represent a worst case scenario and therefore would lead to the derivation of more protective values. For substances for which the bioavailability is dependent on the total organic carbon (TOC) of the sediment, the variability introduced by the presence of toxicity values generated at different TOC concentrations can be accounted for by normalizing each effect datum to a standard sediment with a default TOC content. The 'standard' EU sediment has a default TOC content of 5%. The 'standard' Swiss sediment representing a worst case scenario has been set at 1% TOC (approx. a 10th percentile of OC content measured in Swiss sediments).

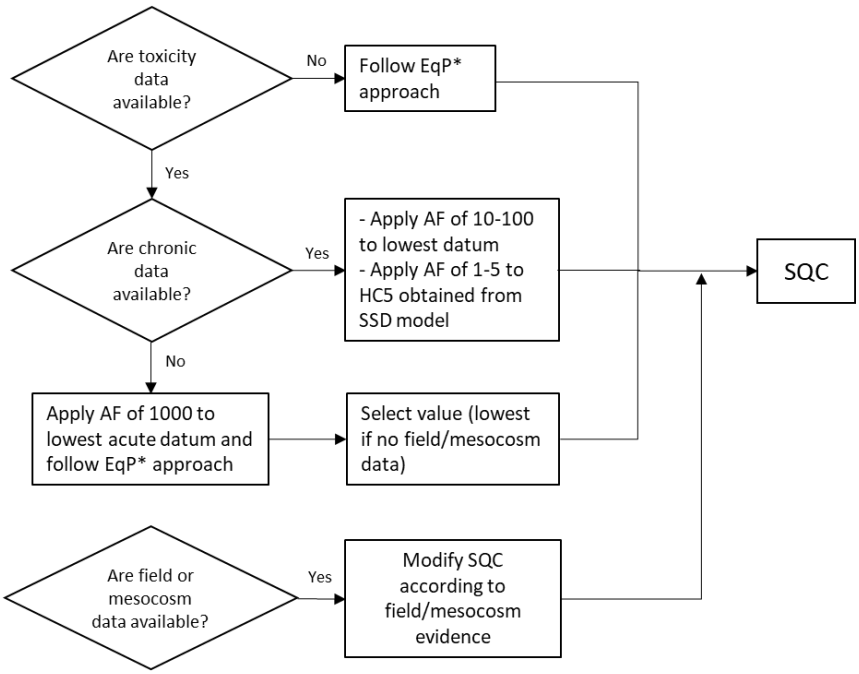


Figure 11: Process for the derivation of SQC (EC 2018). * indicates that the application of an additional AF of 10 is required for substances with log Kow > 5.

References to Annex 3

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Annex 4: Effect concentrations accompanying preliminary SQC

If a SQC is exceeded, effects in the environment cannot be excluded. Table 15 includes reliable effect concentrations for relevant benthic organisms that can be used to assess potential toxic effects associated with measured concentrations in field sediments. If concentrations are below the No Observed Effect Concentrations (NOECs), it is assumed that chronic effects are not likely to occur. If acute effect/lethal concentrations causing 50% of mortality / effect (L/EC50) values are exceeded, acute effects are likely. It is noted that these effect concentrations relate to the test species.

Table 15: Ecotoxicological information for substances with preliminary SQC. NOEC: no observed effect concentration; L/EC50: effect concentration causing 50% of mortality or effect. All concentrations normalized for a standard sediment with 1% organic carbon.

Substance	**Preliminary SQC (µg/kg d.w.)**	**Lowest reliable $NOEC_{chronic}$ (µg/kg d.w.)**	**Lowest reliable LC (or EC) 50_{acute} (µg/kg d.w.)**
Chlorpyrifos	0.03	Not available	27.8 (10 d EC50 for growth of *Hyalella azteca*) 66 (10 d LC50 for survival of *Chironomus dilutus*)
Cypermethrin	0.018	1.79 (60 d NOEC for development of *Chironomus dilutus*)	0.33 (10 d EC50 for growth of d'*Hyalella azteca*) 3.16 (10 d LC50 for survivval of *Chironomus dilutus*)
PFOS	2.7	270 (22 d to 5 week NOEC for survival and sexual maturation of male marine amphipods *Monoporeia affinis*)	Not available
EE2	0.001	4580 (28 d NOEC for reproduction and biomass of the oligochaete *Lumbriculus variegatus*)	Not available
Triclosan	67.4	6740 (28 d NOEC for survival of the oligochaete *Limnodrilus hoffmeisteri*)	Not available
HCBD	2.4	Not available	2400 (10 d NOEC for survival of the amphipod *Hyalella azteca*)

Annex 5: Information on natural background concentrations of trace metals in Switzerland

Table 16 : Range of values of natural and ambient concentrations in Swiss sediments compared to concentrations of metals in upper continental crust (from Taylor and McLennan 2009) and shale (from Salomons and Förstner 1984). Concentrations expressed as mg/kg dry weight.

Metal	Concentrations FOREGS[(a)] floodplain (< 2 mm) (Max-Min; Average)	Concentrations FOREGS[(a)] stream (< 150 µm) (Max-Min; Average)	Natural concentrations in lakes	Ambient concentrations	Upper continental crust	Shale	5th percentile of data base of Swiss sediments
Cd	--	--	0.1-0.5	0.14-0.5	0.098	0.22	0.14
Cr	15-45; 21.8	15-45; 24.8	25-50	18-80	83	90	23.2
Cu	12-54; 21.7	5-27; 15.3	15-50	13-50	25	45	13.1
Hg	0.010-0.028; 0.086	0.006-0.008; 0.037	0.02-0.2	0.03-0.2	--	0.18	0.03
Ni	16-21; 23.9	9-34; 22.1	40-84	14-50	44	68	17.0
Pb	12-164; 38.0	8-343; 48.0	10-50	11-50	17	20	11.2
Zn	40-138; 81.8	30-206; 76.1	40-100	51-100	71	95	51.1

(a) FOREGS (http://www.gtk.fi/publ/foregsatlas) provides concentrations for 10 sites for stream sediments (fraction <150 µm) and for floodplain sediments (fraction < 2 mm) after extraction with *aqua regia*. For mercury, the concentrations are measured with AMA (Automatic Mercury Analyzer).

Table 17: Trace metal concentrations measured in sediment cores collected in different Swiss lakes. Concentrations expressed in mg/kg dry weight and refer to total sediment.

Site	Date	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Reference	Comments
Lake Zurich	Ca.1800	<0.2	--	22	0.2	--	10	50	Von Gunten et al. (1997)	One core, one site Extraction $HNO_3/HClO_4/HF$
Lake Quatre-Cantons	Ca.1700 [(a)]	0.5	--	30	--	--	40	100	Spadini et al. (2003)	One core, one site Extraction HNO_3/H_2O_2
Lake Quatre-Cantons	Ca.1850	--	--	--	0.03	--	22	--	Thevenon et al. (2011)	Extraction $HNO_3/HClO_4/HF$
Lake Constance	Before 1900[(b)]	0.1	50	28	0.1	84	10	58	Müller et al. (1997)	One core, one site
Lake Constance	[(c)]	0.1	39	34	0.05	48	20	53	Wessels (2006)	Avera of values from 3 to 7 m depth
Greifensee	Ca.1928	--	--	15	--	--	15	40	Imboden et al. (1980)	Estimated values from graph
Lake Zoug	Ca. 1800	--	--	--	--	--	16	--	Moor et al. (1996)	Twelve cores in a transect, background determined from one core
Lake Baldegg	Ca. 1800	--	--	--	--	--	13	--	Moor et al. (1996)	Median of 9 cores
Meidsee	Ca. 1850	--	25	30	0.02	--	19	90	Thevenon et al. (2011)	Extraction $HNO_3/HClO_4/HF$
Lake Cadagno	Before 1850	0.4	40	50	--	40	20	100	Birch et al. (1996)	Extraction HNO_3
Lake Geneva	Ca. 1750 [(d)]	0.2	68.2	30.7	0.028	71	18.2	71.0	Tosono (2017)	One core, one site Extraction HNO_3 (OSol)

[(a)] Exponential increase from 1800 to 1850.
[(b)] Avera of samples from before 1900 (24-40 cm).
[(c)] Average from 3 to 7 m depth.
[(d)] ~ 1000 for Hg.

References to Annex 5

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