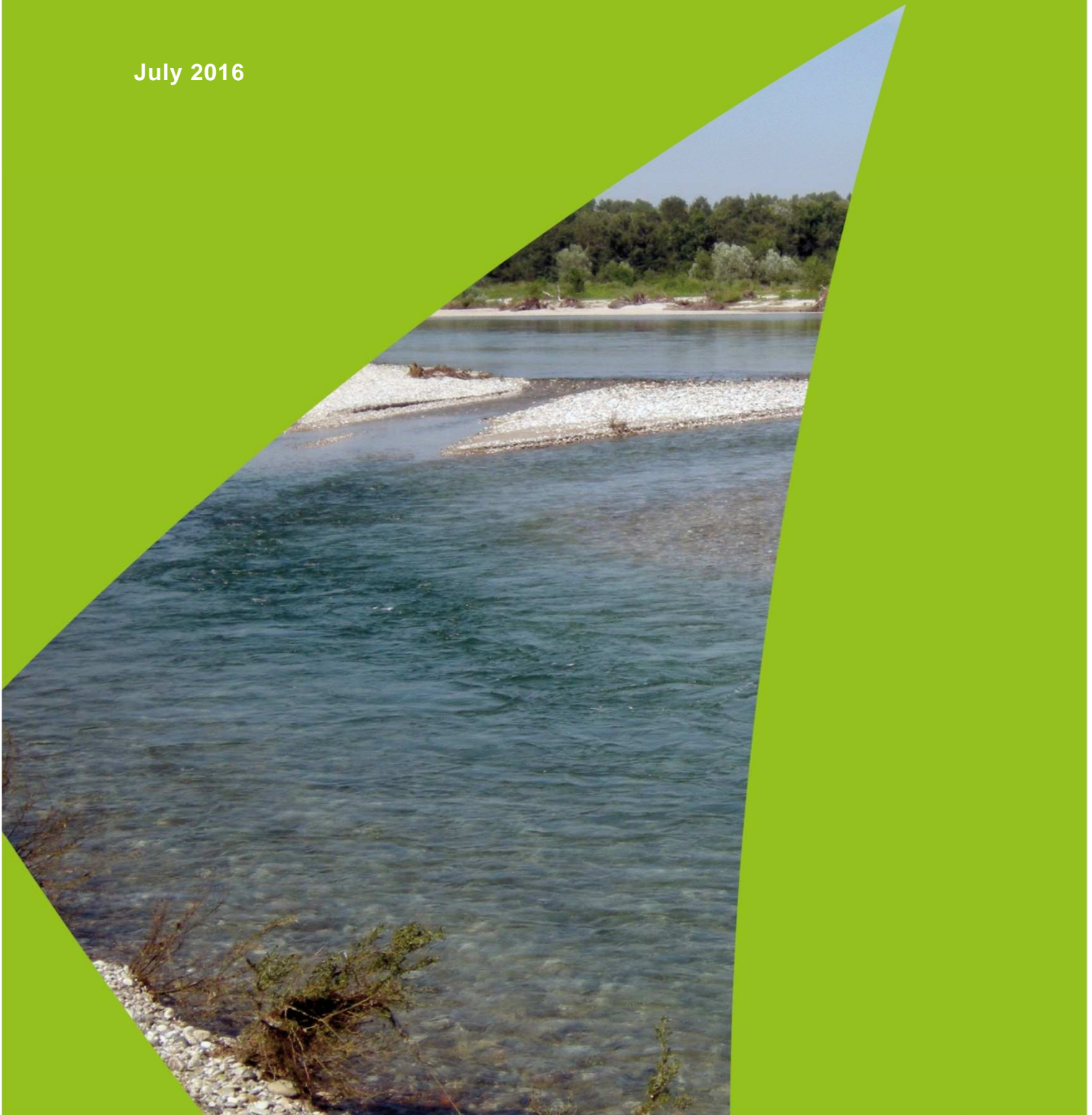




Trace metals in sediments from Switzerland

Situation analysis and recommendations

July 2016



Imprint

Publisher

Centre Ecotox/Oekotoxzentrum, Swiss Centre for Applied Ecotoxicology Eawag-EPFL, EPFL-ENAC-IIE-GE, Station 2, 1015 Lausanne, Switzerland

Authors

Carmen Casado-Martinez, Benoit JD
Ferrari, Etienne Vermeirssen, Inge
Werner

Centre Ecotox/Oekotoxzentrum, Swiss Centre for Applied
Ecotoxicology Eawag-EPFL

Scientific Support

Laboratoire central environnemental (CEL), EPFL
CH-1015 Lausanne

Felippe de Alencastro

Institut national de recherche en sciences et technologies pour
l'environnement et l'agriculture (IRSTEA)
69616 Villeurbanne Cedex (France)

Marc Babut

Institut des dynamiques de la surface terrestre (IDYST), UNIL
CH-1015 Lausanne

Nathalie Chèvre

Interkantonales Labor, Canton de Schaffhouse
CH- 8201 Schaffhausen

Frank Lang

Institut F.-A. Forel, Université de Genève
CH- 1290 Versoix

Jean-Luc Loizeau

e-dric
CH- 1015 Lausanne

Luca Rossi

Laboratoire de la protection des eaux et du sol (GBL), Canton de Berne
CH- 3014 Berne

Rico Ryser

Soluval Santiago
CH- 2108 Couvet

Sergio Santiago

Hydrobiologiste
CH- 1207 Genève

Régis Vivien

Acknowledgement

The authors acknowledge all the cantonal offices that participated in the questionnaire and made their data available for this study; and Sophie Campiche and Rebeca Flück who initiated the Project.

Contact

Carmen Casado: carmen.casado@centreecotox.ch

Citation Proposal

Casado-Martinez C, Ferrari BJD, Vermeirssen E, Werner I. 2016. Trace metals in sediments from Switzerland: situation analysis and recommendations. Swiss Centre for Applied Ecotoxicology Eawag-EPFL, Lausanne.

Oekotoxzentrum | Eawag | Überlandstrasse 133 | Postfach 611 | 8600 Dübendorf | Schweiz
T +41 (0)58 765 55 62 | F +41 (0)58 765 58 63 | info@oekotoxzentrum.ch | www.oekotoxzentrum.ch

Centre Ecotox | EPFL-ENAC-IIE-GE | Station 2 | CH-1015 Lausanne | Suisse
T +41 (0)21 693 62 58 | F +41 (0)21 693 80 35 | info@centreecotox.ch | www.centreecotox.ch

Oekotoxzentrum | Eawag | Überlandstrasse 133 | Postfach 611 | 8600 Dübendorf | Schweiz
T +41 (0)58 765 55 62 | F +41 (0)58 765 58 63 | info@oekotoxzentrum.ch | www.oekotoxzentrum.ch

Centre Ecotox | EPFL-ENAC-IIE-GE | Station 2 | CH-1015 Lausanne | Suisse
T +41 (0)21 693 62 58 | F +41 (0)21 693 80 35 | info@centrecotox.ch | www.centrecotox.ch



Summary

In Switzerland sediments are considered, from a legislative point of view, as part of the surface waters and they must not accumulate persistent pollutants in order to ensure the protection of aquatic life. However, monitoring programmes are not implemented on a pan-national level, and no harmonised recommendations and quality standards for *in situ* sediment assessment are available to date. The results of a questionnaire submitted to the Swiss cantonal offices for environmental protection highlighted that the most common approach for evaluating sediment quality is based on chemical measurements.

As an initial step to assess the quality of Swiss sediments we created a database with results from sediment surveys carried out from 1990 to 2011; most of the data we obtained are for metals. This report summarizes the situation analysis of sediment metal (Cd, Cr, Cu, Hg, Ni, Pb and Zn) concentrations in Switzerland following a preliminary evaluation performed for Cu and Ni (Flück et al. 2012). For these seven metals we provide an overview of the distribution of measured ambient concentrations in surface sediments and its ecotoxicological potential according to existing numerical sediment quality guidelines. Threshold effect concentrations (TEC) and probable effect concentrations (PEC) were also used to provide an overview of spatial and temporal patterns of the potential ecotoxicological properties of sediments. Two additional sets of reference values used by Swiss cantonal agencies for the interpretation of chemical sediment concentrations are considered: 1) reference values recommended by the Swiss “Ordonnance sur la protection des sols”, which are the most common values used by Swiss cantonal agencies for the interpretation of measured sediment concentrations; 2) objectives of the International Commission for the Protection of the Rhine (ICPR, 2007). Metal concentrations were also compared to available data on background levels to help identify anomalies and metals of concern.

The situation analysis performed on the data set shows that there is still an important area of Switzerland for which no data on sediment concentrations are available. Where available, the distribution of sites with concentrations exceeding the limit for probable effects on benthic organisms is apparently random for most metals, suggesting that the sites correspond to hot spots associated with anthropogenic sources rather than relatively high natural background concentrations associated with regional geochemical features. Nevertheless, due to the small data set available as well as its patchy distribution, it is currently not possible to identify geographical trends within Switzerland in terms of geochemical properties, and to define their corresponding background or baseline concentrations with confidence. The exception is a high incidence of Ni concentrations above the limit for probable ecotoxicological effects in canton Geneva, which is in agreement with the previously observed high incidence of exceedances of indicative values for soils in this canton. The available data on natural background concentrations of Ni (and to a lesser extent of Cr) suggest that the TECs for these two metals should be used with care.



The other metals were classified into four separate groups according to their exceedance of respective PEC values: Cd, with only 1% of data above its PEC; Hg with 3% of data above its PEC; and Cu, Pb and Zn with 6% of the data above respective PECs. The general trends over the last decade indicate a decrease in sediment metal concentrations across regions considered so far, with a progressive downshift in the classification of samples to lower priority categories.

We conclude that the prioritisation of metals according to the risk posed to benthic ecosystems should take into account incidence and extent of exceedance of sediment quality guidelines but also the relative contribution of natural background concentrations to the identified risk. The risk posed by some metals such as Hg through bioaccumulation and secondary poisoning through ingestion of contaminated prey should be also considered when the quality criteria used for prioritisation does not take into consideration these type of effects.



Content

1	Introduction.....	1
2	Approach.....	2
2.1	Dataset.....	2
2.2	Exploratory multivariate analysis.....	2
2.3	Ecotoxicological evaluation.....	2
2.4	Comparison with other sediment quality guidelines in use.....	4
2.5	Background concentrations.....	4
3	Results and Discussion.....	6
3.1	General information of the dataset.....	6
3.2	Exploratory multivariate analysis.....	9
3.3	Ecotoxicological evaluation.....	11
3.4	Comparison with other sediment quality guidelines in use.....	12
3.5	Spatial trends.....	12
3.6	Temporal trends.....	22
3.7	Natural background concentrations of metals.....	24
3.7.1	Natural concentrations.....	25
3.7.2	Ambient concentrations.....	25
3.7.3	Geological contribution.....	26
3.7.4	Relevance of EQGs compared to natural background.....	26
4	Conclusions.....	30
5	Recommendations.....	30
6	References.....	31
7	Indices 34	
7.1	List of Figures.....	34
7.2	List of Tables.....	35



1 Introduction

Many contaminants, including metals and organic compounds, have a high affinity for particulate matter. For this reason, many pollutants that enter the aquatic environment accumulate in bottom sediments. Because many of these compounds do not easily degrade, they can persist for a long time in sediments and alter the community living within or in close contact with them. According to the Swiss Water Protection Ordinance (OEaux; OFEV 1998a) the water quality shall be such that: the water, suspended matter and sediments contain no persistent synthetic substances to ensure the protection of aquatic life. A national program for the monitoring of sediment quality with respect to chemical contaminants does not exist, however, several cantonal agencies have carried out studies addressing sediment quality in Switzerland (Flück et al. 2011).

In 2010, an informal working group was created by the Swiss Centre for Applied Ecotoxicology Eawag-EPFL (Ecotox Centre) to discuss sediment quality in Switzerland from a pan-national perspective. Results of a questionnaire sent to and completed by the cantons provided an overview of the expertise available and regulatory needs and priorities in this field. It also allowed to compile available data of chemical concentrations of pollutants measured in sediments (Flück et al., 2012a).

This report summarizes the currently available data on metal concentrations in sediments of Switzerland, focusing on Cd, Cr, Cu, Hg, Ni, Pb and Zn. We provide an overview of the distribution of metals in surface sediments and their ecotoxicological potential based on existing numerical sediment quality guidelines. Results can assist in prioritizing metals and regions of concern, under consideration of natural (background) concentrations in Switzerland, and will provide valuable information for the future development of sediment quality criteria.

It should be noted that the situation analysis addresses this set of metals because they are the most commonly quantified compounds in Swiss sediments but it does not mean that these contaminants have higher interest or require special attention. Other compounds that are or have been considered include polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). PAHs were not included in this analysis because not enough data exist at this time. For a situation analysis of PCBs and dioxin contamination in Switzerland, the reader is referred to Schmid et al. (2010). Few data exist on other contaminants that may enter the aquatic environment through municipal and diffuse sources and accumulate in sediments such as pesticides, pharmaceuticals or personal care products. Questions addressed in this study:

- Can we perform a situation analysis of sediment metal contamination for Switzerland with the available data?
- How do data coming from different studies/cantons compare?
- What is the distribution of metal concentrations in Swiss sediments?
- Are these concentrations ecotoxicologically relevant?
- Are natural background concentrations of metals in sediments an important factor to be considered for an ecotoxicological evaluation?



2 Approach

2.1 Dataset

The data on sediment contamination in Swiss streams and other water bodies were obtained from different sources. Most of the data were obtained from cantonal agencies, either directly in the form of printed reports or retrieved from their web sites. Additional data were obtained from scientific papers (including grey literature) or reports from international commissions. Data were added to the database if the source was considered reliable, even when extraction and quantification methods differed between studies or details on methods were absent.

Several sites have multiple entries, as they have been sampled repeatedly over the years. All entries were used for the statistical analysis, whereas only the most recent data were used for the cartographic representations. For the statistical analyses, data below the detection limit were set to a value of half of the limit of detection (LOD) of the analytical method, which varied from study to study.

2.2 Exploratory multivariate analysis

Principal component analysis (PCA) using the Varimax rotation method and the SPSS software was used to explore correlations among metals in the raw data matrix. Significant correlations between variables (Bartlett's test of sphericity, $p < 0.001$) and the Kaiser-Meyer-Olkin measure of sampling adequacy (0.643) indicate that reducing the number of variables into principal components was a valid approach to analyse the dataset.

Two principal components (F1, F2) explained more than 76 % of the total variance in the dataset. The distribution of the sites in the space defined by these two factors was therefore further explored. One defined group consisted of two samples with a high contribution of F2 and no contribution of F1, and a sample with a high contribution of F1 and no contribution of F2. Since these samples could have disproportionately influenced the result of the PCA, a subsequent analysis excluded these samples. The results of this second analysis were similar to those obtained in the first including all data, thus the first analysis was retained.

2.3 Ecotoxicological evaluation

Metal concentrations measured in sediments were interpreted by comparison with the threshold effect concentrations and probable effect concentrations (TEC and PEC, respectively; MacDonald et al. (2000)). These numerical values have been developed for each metal using a consensus approach among different types of empirical and mechanistic sediment quality guidelines (SQGs). Flück et al. (2012) and Wenning et al. (2005) provide an in-depth analysis on the development and selection of SQGs. These SQGs refer to concentrations measured in total sediment.

Sampling sites were classified into three different categories based on measured metal concentrations: 1) samples with concentrations below the TEC are considered of good quality, with low toxic risk; 2) samples of poor quality are those with concentrations above the PEC, indicating a probable toxic risk; and 3) samples with concentrations above the TEC and below the PEC are considered of medium quality. Note that the application of these guidelines was carried out independently of sediment properties. Given that the data dominantly consist of concentrations measured in the fine sediment fraction, toxicity may be overestimated when compared to TEC and PEC values (which are based on total sediment concentrations).



Five quality categories were used in line with the MSK classification scheme. This can be done using threshold values developed statistically or, as in this case, using arbitrary numerical factors (Tab. 1). This is a pragmatic approach to develop a management tool where categories allow a prioritisation as well as identification of potential reference sites.

In addition to determining if the concentrations of individual metals exceed toxicity thresholds (TEC-PEC), mean quotients (m-PEC-q, see box 1) were calculated by dividing the sediment concentrations by the respective PEC and then calculating the mean of the quotients for the individual metals. The resulting quotient provides a method of accounting for both the presence and the level of concentrations of multiple chemicals in sediments relative to the PEC. Both the incidence and magnitude of toxicity in laboratory toxicity tests and the impairment of benthic communities increase with an increasing m-PEC-q. It is considered an effect-based index that estimates the likelihood that a sediment would be toxic to sediment-dwelling organisms. This concentration-response relationship has been used to develop threshold values for the classification of sediments into five categories, each with increasing incidence of toxicity to benthic invertebrates (Ingersoll et al., 2001). The use of this categorical classification, however, entails some degree of uncertainty because the categories were defined for mean quotients that consider in its development the contribution of additional types of contaminants that we do not include in this study (e.g. PCBs and PAHs). We only calculated the mean quotient if the number of metals for the entry was at least five.

In addition to the categorical classification system developed from US data we used the threshold values developed empirically by Vivien et al. (2011) by matching mean quotients for the set of metals considered here and the oligochaete index (IOBS) as a measure of the alternation of the local oligochaete community for a number of sites in canton Geneva (Tab. 1). These classification criteria have been also developed using the same set of SQGs (TEC and PEC) for calculating the mean quotients but the concentration-response relationship used for the development of thresholds for categorical classification only considers metal concentrations with no contribution to the response observed (the IOBS index) of other compounds that could be present. Because the measurement endpoint considered for its development is different the ecotoxicological potential of sediments refers only to the oligochaete community.

Tab. 1: Different criteria used for the classification of samples into quality classes. C: measured concentration of each metal; TEC/PEC: threshold and probable effect concentrations for each metal; m-PEC-q: mean quotient calculated using PEC values; m-TEC-q: mean quotient calculated using TEC values. See text for detailed explanation.

3 categories		5 categories	
TEC/PEC		m-PEC-q	
		Ingersoll et al. 2001	Vivien et al. 2011
	C < 1/2 TEC	m-PEC-q < 0.1	m-PEC-q < 0.13
C < TEC	1/2 TEC < C < TEC	0.1 < m-PEC-q < 0.5	0.13 < m-PEC-q < 0.19
TEC < C < PEC	TEC < C < PEC	0.5 < m-PEC-q < 1.0	0.19 < m-PEC-q < 0.3
C > PEC	PEC < C < 2*PEC	1.0 < m-PEC-q < 5.0	0.3 < m-PEC-q < 0.4
	C > 2*PEC	m-PEC-q > 5.0	m-PEC-q > 0.4



2.4 Comparison with other sediment quality guidelines in use

Different sets of reference values used by Swiss cantonal agencies for the interpretation of chemical concentrations measured in sediments have been also considered here (Flück et al., 2012b): the reference values recommended by the Swiss “Ordonnance sur la protection des sols” (OSol, OFEV, 1998b), which are the most common values used by Swiss cantonal agencies for the interpretation of sediment concentrations, and the target values of the International Commission for the Protection of the Rhine (ICPR, 2007), which are used to define the lowest priority category for suspended matter/sediments from the Rhine. For the assessment of sediment contamination, relevant sediment pollution is attributed to concentrations fourfold the ICPR target value. Each of these sets of values have different management objectives.

2.5 Background concentrations

Natural background concentrations may exist to which local organisms are well adapted. In this case, the use of SQGs derived elsewhere would lead to unrealistic risk evaluation results. We evaluated the data to examine if such natural background concentrations may exist in sediments of Switzerland, and what influence these may have on the interpretation and risk assessment of metal concentrations measured in sediments.

For this, we compiled three different types of data relevant for evaluating the natural contribution to metal concentrations in sediments, including natural (background) concentrations measured in (pre-industrial) sediments and concentrations that are statistically representative of environmental concentrations not affected by anthropogenic sources of pollution. The resulting background concentrations came mainly from lakes, where studies have addressed historical contamination in sediment cores. When sediment cores were available, the concentrations retained as background values were ideally those measured in the layer dated ca. 1850. Other reference values from large datasets from Switzerland that have been used previously for the interpretation of measured metal concentrations in sediments are also considered, including the concentrations in stream sediments reported for Switzerland in the atlas of the Forum of the European Geological Surveys¹ (Salminen 2005), which has been most commonly used as default methodology are also considered. Average concentrations in different types of rocks have been also considered as indicative of the regional geochemistry.

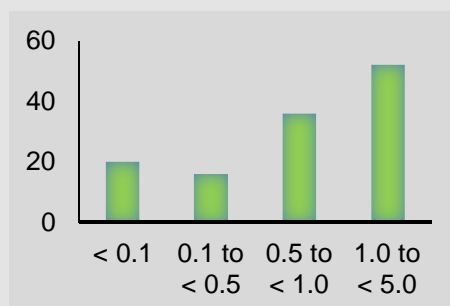
¹ www.gsf.fi/publ/foregsatlas



BOX 1: CALCULATION AND USES OF MEAN QUOTIENTS FOR SEDIMENT QUALITY CLASSIFICATION

Numerical effect-based sediment quality guidelines (SQGs) have been developed over the past 20 years to aid in the interpretation of the relationships between chemical contamination and measures of adverse biological effects. Different methodologies have been used for their development, as they have different narrative intent. Any regulatory body considering the adoption of an environmental quality paradigm involving the use of SQGs should initially identify the specific regulatory objectives and desired environmental management and quality goals, since they will influence the decision of adopting SQG values from other governments or the derivation of different values that are thought to be more ecologically relevant to the environmental conditions that the regulatory agency is charged to protect. The approach used for developing SQGs should be based on the identified relevant receptors (i.e., sediment-dwelling organisms, wildlife, or humans), the degree of protection to be afforded, the geographic area to which the values are to be applied (i.e., site-specific, regional, or national), and their intended uses (e.g., as informal screening tools, enforceable standards, or remediation objectives). In practice, regulatory agencies in many countries have adopted SQGs from North America without adequate consideration of environmental differences that might make such guidelines more or less relevant. Different exercises have studied the performance of different SQG approaches and the predictive ability with respect to biological effects. In addition, several regional and national agencies have developed frameworks to help deciding whether recalibration of SQGs approaches for regional data improves the performance and predictive ability of SQGs developed elsewhere.

- *Derivation of m-SQG-q*: each chemical concentration in a sample is divided by its respective SQG, resulting in an individual ratio of the concentration of that chemical in the sample to its respective SQG. Then, all resulting quotients either for all individual chemicals or several chemical classes are summed. The individual quotients can be summed for classes of chemicals, typically including trace metals, polycyclic aromatic hydrocarbons, and chlorinated organic hydrocarbons. This second approach tends to reduce variability in concentration-response relationships where individual SQGs differed in predictive ability. Finally, either the sum of the individual quotients is divided by the number of SQGs or the sums of the three classes are divided by three to derive the m-SQG-q value for each sample.
- *Attributing probability of sediment toxicity*: the probability of observing sediment toxicity can be estimated by comparing m-SQG-q to previously published probability tables or, preferably, by establishing site-specific exposure-response relationships. Alternatively, regression equations that have been developed to characterize concentration-response relationships can be used.
- *Calibration or downscaling to regional/ local conditions*: Concentration-response relationships developed from large-scale assessments often improve as the data set is focused down to smaller areas. Accordingly, the predictive ability of some SQGs differ when applied to data from different regions due to geochemical factors, differences in the sensitivity of methods used to measure biological effects, or due to differences in the nature of the chemical mixtures between sites or regions. The approach from several agencies has been to recalibrate SQGs approaches within smaller areas with site-specific studies of their predictive ability because such approach increases the confidence in the use of SQGs in management decisions. Matching results of toxicity tests and/or benthic community composition analyses are needed for performing such type of exercise. Examples of this approach can be found in Field and Norton (2014) and Bay et al. (2012).



Incidence of toxicity in acute amphipod survival tests over ranges in m-PEC-q calculated for US freshwater sediments (from Ingersoll et al. 2001).



3 Results and Discussion

3.1 General information of the dataset

The sediment chemistry data was compiled from studies carried out from 1990 to 2011. A data base with 607 entries was generated. In the absence of harmonised recommendations for sediment sampling, sample preparation and chemical analyses, the database showed great heterogeneity among studies and cantons in terms of fraction and extraction technique used prior to metal quantification (Tab. 2). Most data correspond to measurements on the grain size fraction < 0.063 mm and to a much lesser extent < 2 mm. Similarly, less than half of the total number of entries correspond to data obtained using microwave extraction with a mixture of HCl and HNO₃ or aqua regia. For some data the fraction analysed and the extraction procedure are not reported. For this reason, the use of data on the fine fraction and total extraction may lead to overestimation of toxicity when compared to TEC and PEC values.

Table 3 shows a summary of the statistics used to analyse the available data and the classification of metal concentrations into three quality classes defined by the corresponding TEC-PEC values. The number of entries varies among compounds from 488 to 607, with the highest number of entries for Cu, Ni, Zn and Pb and the lowest for Cd and Cr. Concentrations measured range over one order of magnitude for Hg (< LOD to 7.8 mg Hg/kg dw), two orders of magnitude for Cd, Cr, Ni and Zn (< LOD to 50 mg Cd/kg dw; 7.4 to 247 mg Cr/kg dw; 5.0 to 303 mg Ni/kg dw; 13.3 to 3658 mg Zn/kg dw), and three orders of magnitude for Cu (1.3 to 1068 mg Cu/kg dw) and Pb (4.6 to 1287 mg Pb/kg dw).

Tab. 2: Sediment fraction and extraction method used prior to quantification of metal concentration in sediments.

	Database entries (%)
Sediment fraction	
< 2mm	12
< 0.063 mm	82
n.a.	6
Extraction method	
HCl-HNO ₃ microwave	39
Unknown	61

For all metals, the mean concentration is higher than the median, and the 90th percentile is much lower than the maximum value. The distribution is skewed to the right and fits a lognormal distribution (see Fig. 1), common when studying the distribution of contaminants in the environment. This distribution is characterised by large differences between the mean and the median, this last one less influenced by high-range data. This difference is much higher for Zn, Cd, Cu and Pb, whereas the difference for Ni and Cr is much lower. This indicates that Ni and Cr distributions – compared to other metals – are less influenced by few data in the highest range likely associated with anthropogenic pollution. The dispersion (ratio percentile 90%/ 10%) for Cr and Ni is also minimal (~ 3), and maximal for Hg and Pb (10.3 and 7.15, respectively).



Tab. 3: Descriptive statistics of sediment metal concentrations in the dataset. All data expressed as mg/kg dry weight. C means measured concentration. LOD is method detection limit. Values higher than TEC are underlined, and those higher than PEC are bold.

	Cr	Ni	Cu	Zn	Cd	Hg	Pb
N	488	607	607	593	498	559	592
% samples C < LOD	0	0	0	0	13	5	0
Mean	<u>55.3</u>	<u>41.4</u>	<u>60.3</u>	<u>209</u>	0.55	<u>0.25</u>	<u>55.8</u>
SD	26.7	31.1	70.0	251	2.25	0.68	81.7
CV (%)	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
1 %	12.5	12.0	5.25	23.9	0.06	0.01	5.92
10 %	31.5	20.5	18.9	68.9	0.15	0.04	14.4
1 st quartile	38.9	<u>26.5</u>	27.0	97.7	0.25	0.08	23.7
Median	<u>49.5</u>	<u>34.2</u>	<u>42.0</u>	<u>148</u>	0.38	0.12	<u>36.0</u>
3 rd quartile	<u>66.2</u>	<u>45.8</u>	<u>71.6</u>	<u>244</u>	0.51	<u>0.20</u>	<u>61.4</u>
90 %	<u>86.0</u>	<u>63.4</u>	<u>113</u>	<u>378</u>	0.78	<u>0.41</u>	<u>103</u>
99 %	<u>144</u>	<u>193</u>	<u>277</u>	<u>947</u>	<u>2.22</u>	<u>2.46</u>	<u>378</u>
Maximum	<u>247</u>	<u>303</u>	<u>1068</u>	<u>3658</u>	<u>50.0</u>	<u>7.80</u>	<u>1287</u>
Normal distribution ^a	No	No	No	No	No	No	No
Quartile 90% / 10%	2.73	3.09	5.98	5.49	5.20	10.3	7.15
TEC	43.4	22.7	31.6	121	0.99	0.18	35.8
PEC	111	48.6	149	459	4.98	1.06	128
% samples C < TEC	35	15	33	38	95	71	51
% samples TEC < C < PEC	62	66	61	55	5	26	43
% samples C > PEC	3	20	6	7	1	3	6
ICPR target value (TV)	--	50	50	200	1.0	0.5	100
% samples C > TV	--	19	40	33	5	6	11
Osol	50	50	40	150	0.8	0.5	50
% samples C > Osol	39	19	52	48	9	6	33
FOREGS	24.8	22.9	17.9	76.1	--	0.037	26.7
% samples C > FOREGS	76	85	91	85	--	83	67
Pardos et al.	32.3	30.8	27.4	86.3	0.24	0.14	48.0
% samples C > Pardos et al.	71	62	73	80	75	35	34

^a Shapiro Test, p<0.001.

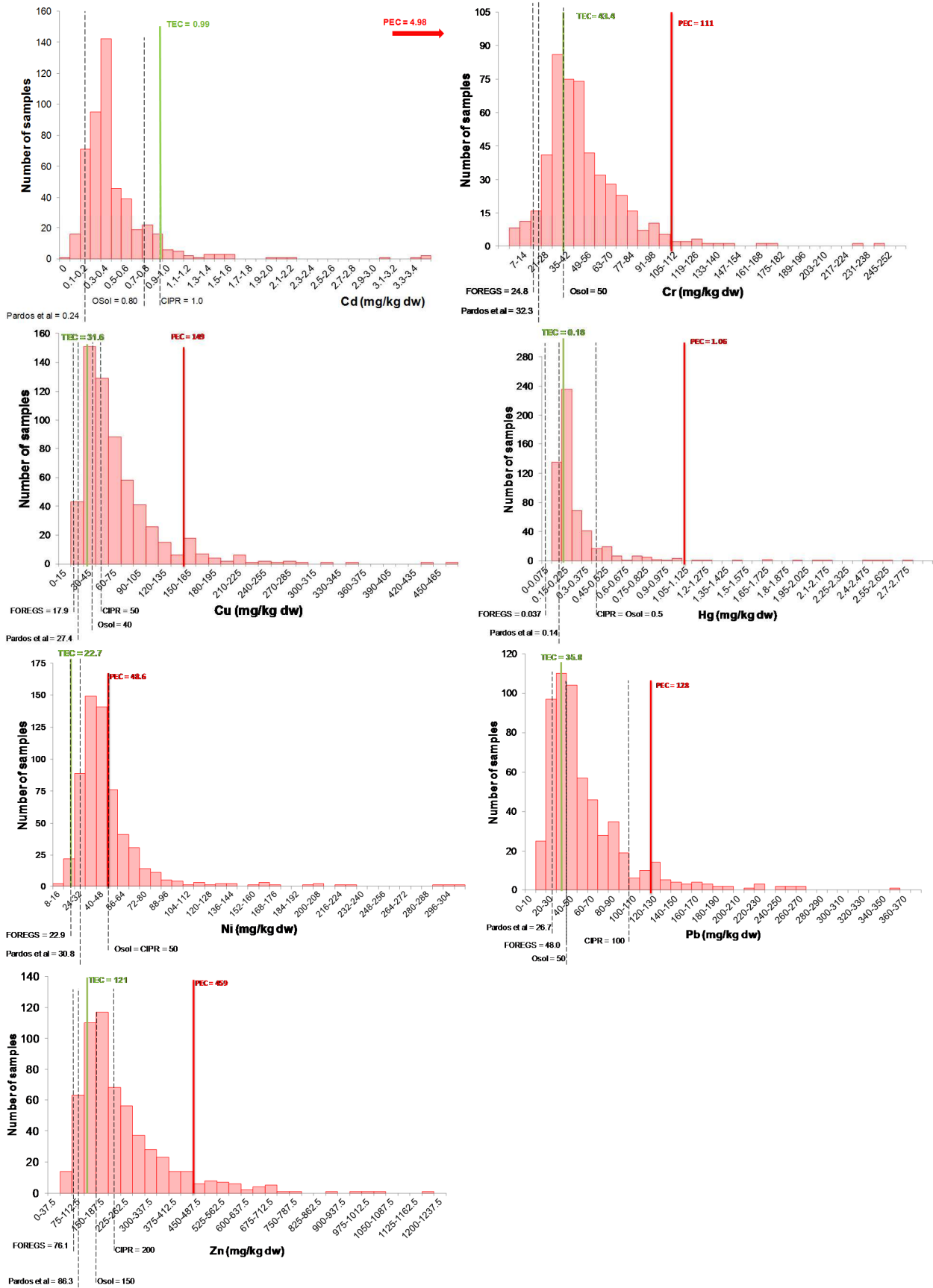


Fig. 1: Distribution of metal concentrations measured in Swiss sediments. The reference values used to classify concentrations according to different criteria are included for comparison purposes. See text for details.



3.2 Exploratory multivariate analysis

According to the scree plot of results we extracted two principal components that explained more than 76 % of the total variance in the dataset. The first extracted factor (F1) explained 46 % of the variance and accounted for Cd, Pb, Zn, and Cu, while the second extracted factor (F2) explained 30 % of the variance and accounted for Ni and Cr (Fig. 2). Mercury was not associated with any of these two factors; an initial analysis showed that a third extracted factor explaining 15 % of the total variance accounted exclusively for Hg (data not shown). The distribution of the sites in the space defined by these two factors (Fig. 3) showed that the samples from Valais (VS) and those from Geneva (GE) have a higher contribution of F2 compared to samples from other cantons. A high correlation between metal concentrations in sediments is the result of one or more factors that the respective metals have in common, for example a natural source. Similarly, the relationships identified by the PCA can be used to differentiate, within a sediment dataset, between locations that display background levels and locations that are potentially impacted. A high correlation is observed between Cr and Ni ($r=0.92$; $p<0.001$) as it resulted in its contribution to F2. Nickel and Cr are a typical example of metals that are commonly correlated in rocks, soils, and sediments, with relatively constant Ni/Cr ratios among rocks classified as granite, shale, clay, and basalt (Fig. 4). The correlation of Ni versus Cr concentrations in the dataset of Swiss sediments follows the same trend with virtually the same slope as the regression for different rocks (Alloway, 1990), with concentrations of Ni and Cr falling within this constant ratio from 10 to 160 mg/kg dw and 7 to 250 mg/kg dw, respectively.

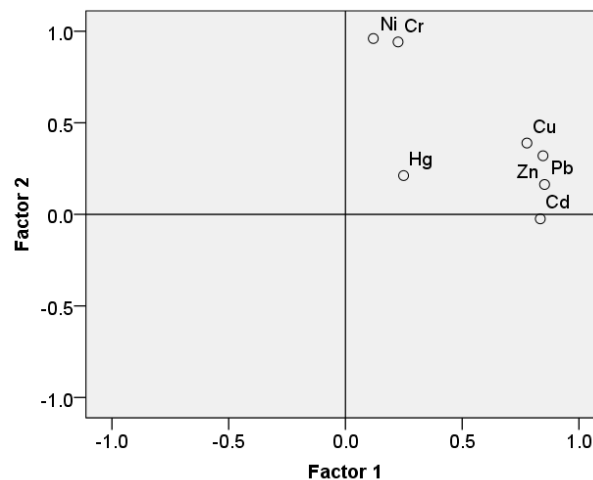


Fig. 2: Component scores for the seven variables.

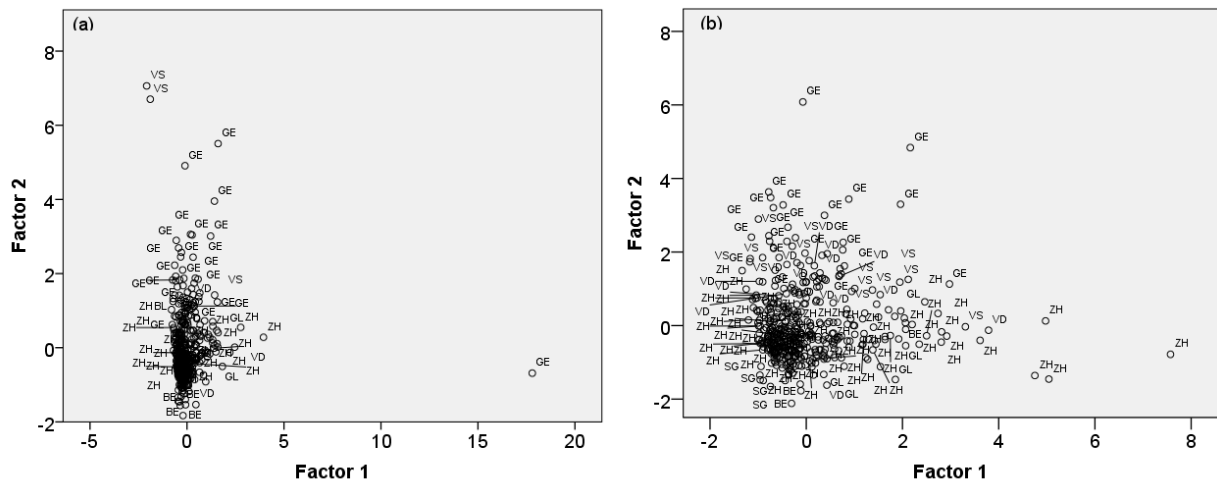


Fig. 3: Factor loadings for the cases included in the initial PCA (a) and when excluding the cases with conspicuous metal concentrations (b).

Relatively constant ratios of one metal to another can be used for background analysis, with metals found at elevated concentrations that do not fit the background ratio indicating an anthropogenic release (e.g. falling out of the 95 % of the confidence limits, or using the Lilliefors test to minimise type I errors among the 5 % of data falling out of the confidence limits (Hou et al. 2009)). The most common element used for such exercises is aluminium, but virtually any metal can be used for this purpose if one can ensure that the high correlation is not due to a common anthropogenic source for these two metals. We cannot preclude an anthropogenic source contributing to both Ni and Cr but, given the range of natural concentrations in rocks and the relatively constant ratio among these two metals in sediments that fit that from rocks, it is probable that the same range of natural variability could be foreseen for sediment concentrations according to the regional geochemistry.

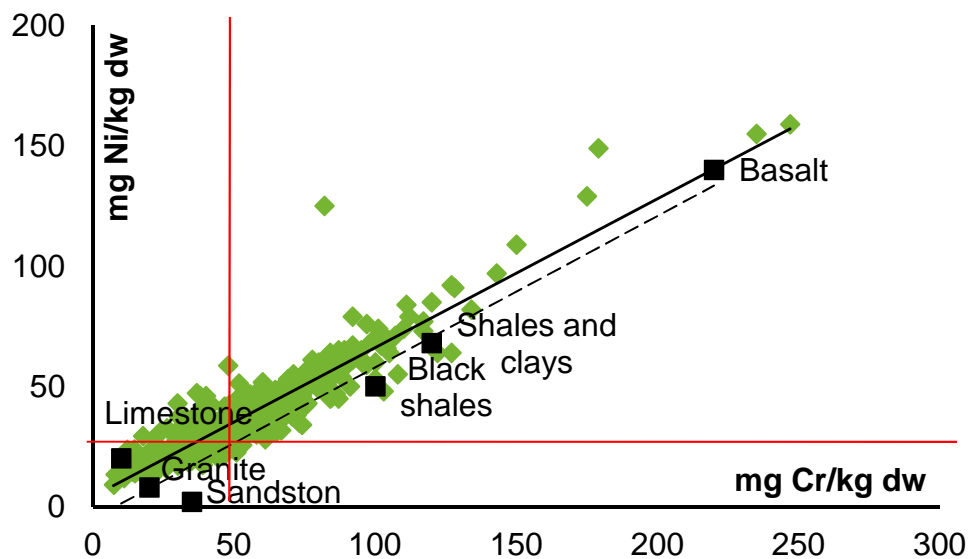


Fig. 4: Correlation plot of nickel versus chromium concentrations in Swiss sediments (solid line) and average concentrations in rocks (dotted line).



3.3 Ecotoxicological evaluation

The order of metals with a higher proportion of samples in the lowest risk category ($C < TEC$) is

$Cd (95 \%) > Hg (71 \%) > Pb (51 \%) > Zn (38 \%) > Cr (35 \%) > Cu (33 \%) > Ni (15 \%)$

Conversely, the highest proportion of samples in the highest risk category is

$Ni (20 \%) > Zn (7 \%) > Pb (6 \%) \sim Cu (6 \%) > Hg (3 \%) \sim Cr (3 \%) > Cd (<1 \%)$.

The mean for all metals except Cd was above the corresponding TEC value. For Cr, Cu, Pb and Zn also the median, the 3rd quartile, 90th and 99th percentile exceeded the corresponding TEC, and for Ni even the 1st quartile exceeded the TEC value. Cd and Hg only exceeded the TEC value at the 99 % and 3rd quartile, respectively. When compared to the PEC value, all metals -except for Cd- exceeded this guideline at the 99 % percentile except Ni, which exceeded the corresponding PEC at the 90 % percentile. Cd did not exceed the PEC even at the 99 % percentile.

Cd is the only metal with the mean and the median concentration below the TEC (0.55 ± 2.25 mg/kg and 0.38 mg/kg, respectively). In fact, 95 % of the total number of data was below the TEC and only 5 % of sites had concentrations above the TEC and below the PEC, corresponding to the intermediate risk category. The PEC value for Cd was not exceeded in any case but one. This indicates that Cd could be considered a contaminant of low concern according to measured environmental concentrations.

For Hg, only 3 % of the data exceeds the PEC, and 26 % of the Hg concentrations are between the TEC and PEC. This is the lowest proportion of samples with intermediate concentrations among the metals considered with the exception of Cd. In spite of this, the mean Hg concentration within the database (0.25 ± 0.68 mg/kg) is slightly above the TEC value but the median is not (0.12 mg/kg).

For Pb the proportion of data below the TEC is about 50 %, 40 % of reported concentrations are higher than the TEC but lower than the PEC, and the remaining 6 % of data were above the PEC. The mean Pb concentration is 55.8 ± 81.7 mg/kg, which is well above the 35.8 mg/kg of the TEC for this metal, while the median (36.0 mg/kg) was around the lowest threshold for toxic effects.

For Cr, Cu and Zn the majority of the measured concentrations in Swiss streams are higher than the TEC and lower than the PEC, with 30 to 40 % of the samples below the TEC and the remaining 3 to 6 % (for Cr, and Cu and Zn respectively) of the samples being above the PEC. As for Pb, the mean and the median concentrations for Cr, Cu and Zn are higher than the TEC value, in the case of Cu and Zn the median is approx. double the TEC.

The metal Ni has the highest proportion of measured concentrations between the TEC and PEC values (66 %), and 20 % of the measured concentrations, which accounts for 119 sites, are above the PEC value. The mean is closer to the PEC than to the TEC (41.6 ± 31.3 mg/kg) whereas the median is 34.2 mg/kg.

It should be noted that Cd and Hg are priority hazardous substances (substance of especial concern) under the WFD whereas Pb and Ni are priority substances. Monitoring and management recommendations should be provided that are in line with the particular classification of each metal compound.



3.4 Comparison with other sediment quality guidelines in use

The use of alternative sediment quality values for the assessment of sediment concentrations results in a different proportion of samples with exceeding concentrations. According to the more stringent nature of the reference value recommended by the Swiss “Ordonnance sur la protection des sols” (OSol, OFEV, 1998b) and the target value of the International Commission for the Protection of the Rhine (TV, ICPR, 2007) compared to the corresponding PEC, a higher proportion of samples are above these guidelines. For example, measured environmental concentrations in the Rhine watershed are compared with the target values, which are used to identify concentrations of low concern. A value of fourfold the target value is used for the identification of relevant pollution. Thus, the ICPR target values would be more in line with the TEC rather than the PEC according to their narrative intent and the corresponding levels of concentrations. Similar considerations apply to the OSol reference values.

The order of metals with a higher proportion of samples with concentrations above the TV is

Cu (40 %) > Zn (33 %) > Ni (19%) > Pb (11 %) > Hg (6 %) > Cd (5 %)

and above the OSol is

Cu (52 %) > Zn (48 %) > Cr (39%) > Pb (33 %) > Ni (19%) > Cd (9 %) > Hg (6 %)

3.5 Spatial trends

To answer the question of whether spatial trends can be identified in metal contamination in sediments, maps showing the classification of sites into the different quality classes defined by the corresponding TEC-PEC values have been derived. They are presented as three or five quality classes in Fig. 5-13.

For most of the metals the distribution of sites with concentrations exceeding the limit for probable effects on benthic organisms is apparently random. 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. On the other side, a high incidence of Ni concentrations above the limit for probable ecotoxicological effects is located in canton Geneva. We cannot preclude an overrepresentation of Ni-contaminated sites in this canton due to different study objectives but the absence of this trend for the other metals and the high incidence of exceedance of indicative values for soils in this canton previously observed by the “Réseau d'observation des sols Genevois” (GEOS, Lamy et al. 2014) indicate that sediments may also have a relatively high background concentration of Ni compared to other regions. A detailed study of available data of background concentrations in sediments is included in section 3.7.

If we compare the maps produced using three or five quality classes we can observe that the use of five quality categories for each metal, with the lowest and highest priority categories separated into two random categories, allows to prioritise the sites with more detail within each region. This classification system, however, is purely a management tool as the newly developed categories do not have any ecotoxicological meaning (except for the intermediate quality class as it is maintained for concentrations between the TEC and the PEC).

Fig. 12 and Tab. 4 shows the classification of sites according to the quality classes defined by the calculated mean quotients of metal contamination and the corresponding probability of toxicity as defined by the thresholds



developed by Ingersoll et al. (2001). The majority of sites is classified as low or medium-low category sites, with a low probability of toxicity. The proportion of sites classified as medium-high priority sites accounts to 20 %. A remaining 4 % of samples are attributed a high priority and no samples were classified in the highest priority category. In summary, one quarter of the samples is considered as medium-high or high priority, and even if this percentage does not seem conspicuous it accounts for almost 150 samples. It should be noted that the quotients were calculated here using only seven metals, but concentration-effect relationships used to derive the threshold for toxicity classification take into account the contribution (presence) of PCBs and PAHs to the observed toxicity. When other compounds are added to the calculation of the quotients a shift into higher or lower priority categories is expected, but the direction of the shift is unknown.

Classification of sites using the threshold values for categorical classification of sites according to the match between metal contamination and the IOBS index (Vivien et al. 2011) shows a different pattern from that obtained by using the ones developed by Ingersoll et al. (2001). Almost half of the samples end up in the highest priority category and a relatively low proportion falls within the two categories of lowest priority (see Fig. 13 and Fig. 14). While the PEC values are the same, the use of a different cause-effect relationship used to develop the quality classes is the reason behind such different classification of sites. In addition, they have different prediction objectives, one being based on the incidence of toxicity in laboratory toxicity tests and the other being based on the incidence of oligochaete community alterations. Whereas the first approach has not been validated or recalibrated for use in Switzerland, the relative sensitivity of the oligochaete index in relation to other effect endpoints has not been established. A recalibration or validation study addressed to establish the predictive ability of SQGs and SQGs approaches for site classification using relevant databases of chemical concentrations and biological effects for sediments in Switzerland should help identifying the most suitable approach for implementation.

Tab. 4: Classification of samples according to the m-PEC-Q values calculated using the measured concentrations of the metals Cd, Cr, Cu, Hg, Ni, Pb and Zn. Classification into classes follows results from Ingersoll et al. (2001).

m-PEC-Q	Nr of samples	% samples toxic to 28d <i>H. azteca</i>	Priority
< 0.1	15 (1%)	10 %	Lowest
0.1 to 0.5	453 (74%)	17 %	Medium-low
0.5 to 1.0	120 (20%)	56 %	Medium-high
1.0 to 5.0	25 (5%)	96 %	High
> 5.0	0 (0%)	100%	Highest

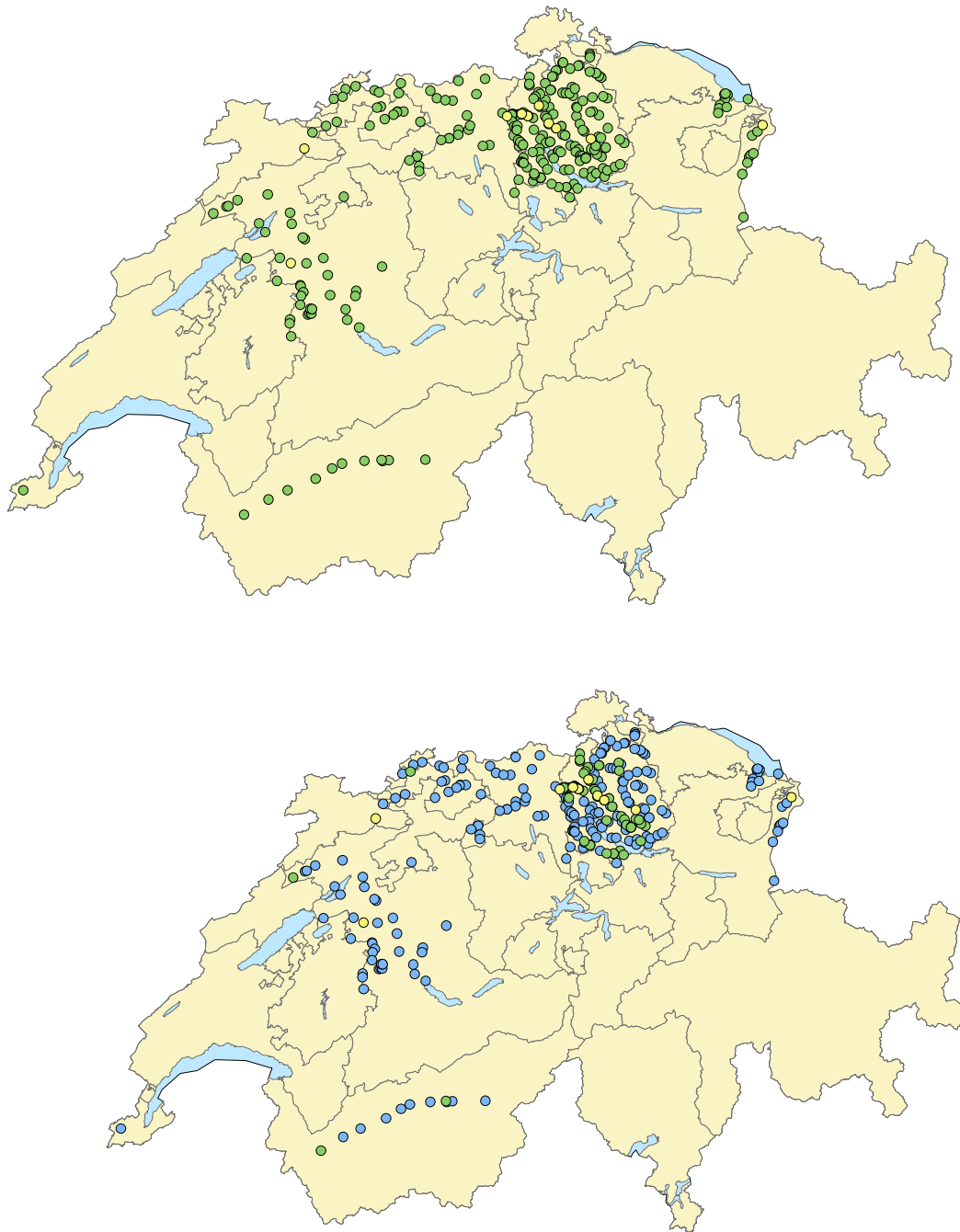


Fig. 5: Cadmium concentrations measured in Swiss sediments classified according to the TEC and PEC in three quality categories (above) and in five categories (below). Categories are explained in Table 1. Source of graphic layer: Swisstopo. Data property: cantons (N=305).

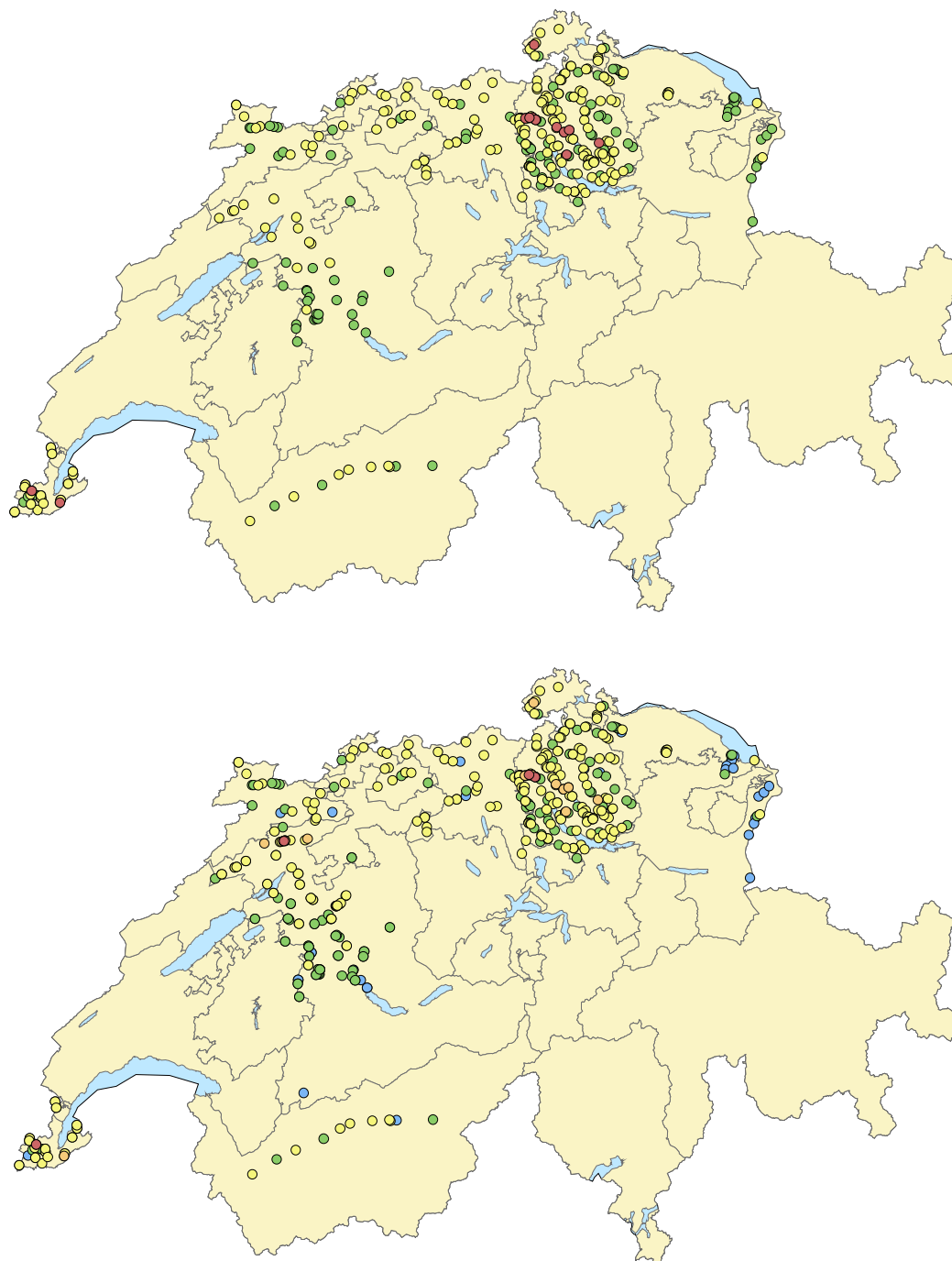


Fig. 6: Copper concentrations measured in Swiss sediments classified in three quality categories according to the TEC and PEC (above) and in five categories as explained in Table 1 (below). Source of graphic layer: Swisstopo. Data property: cantons (N=358).

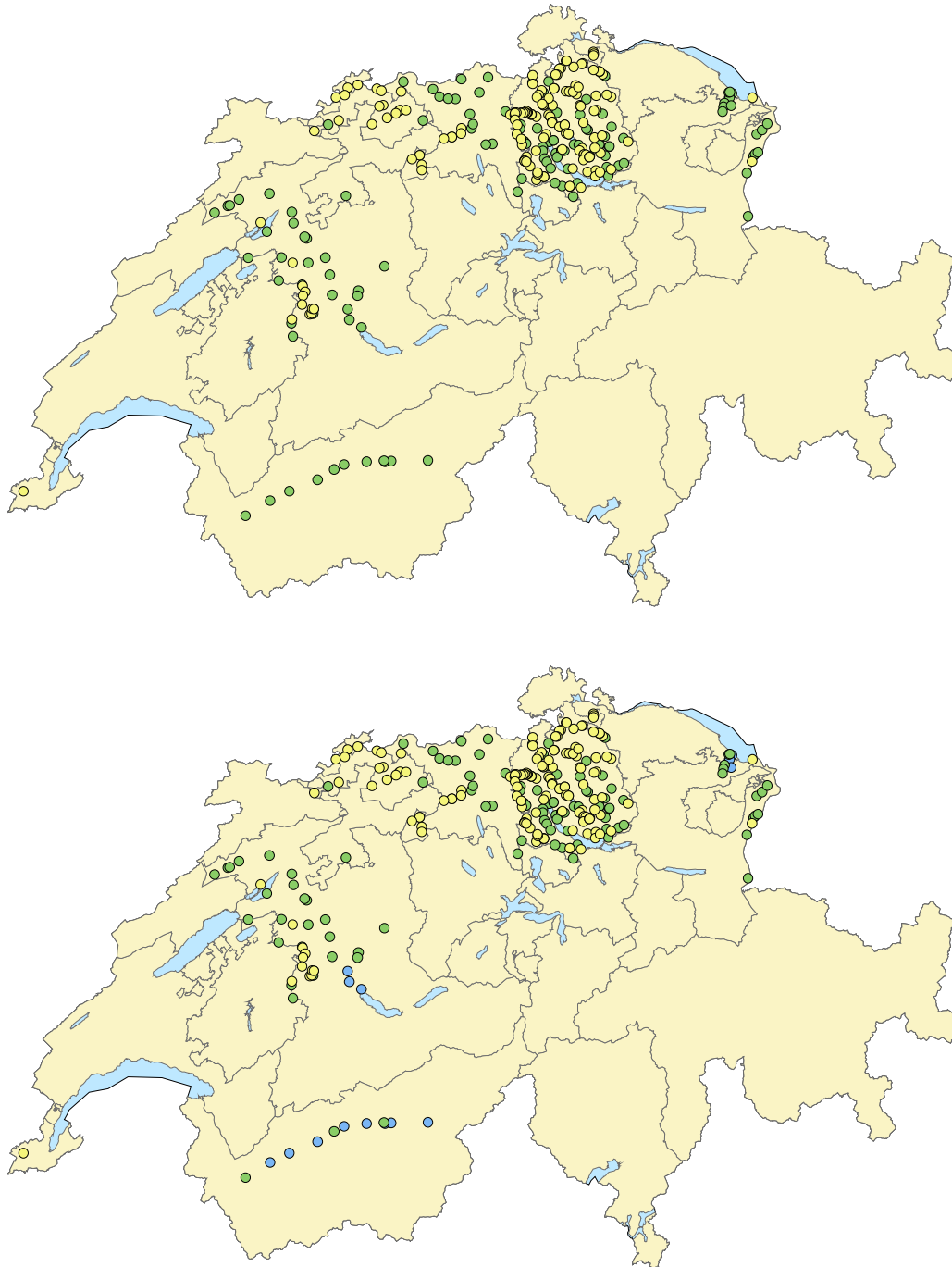


Fig. 7: Chromium concentrations measured in Swiss sediments classified in three quality categories according to the TEC and PEC (above) and in five categories as explained in Table 1 (below). Source of graphic layer: Swisstopo. Data property: cantons (N=298).

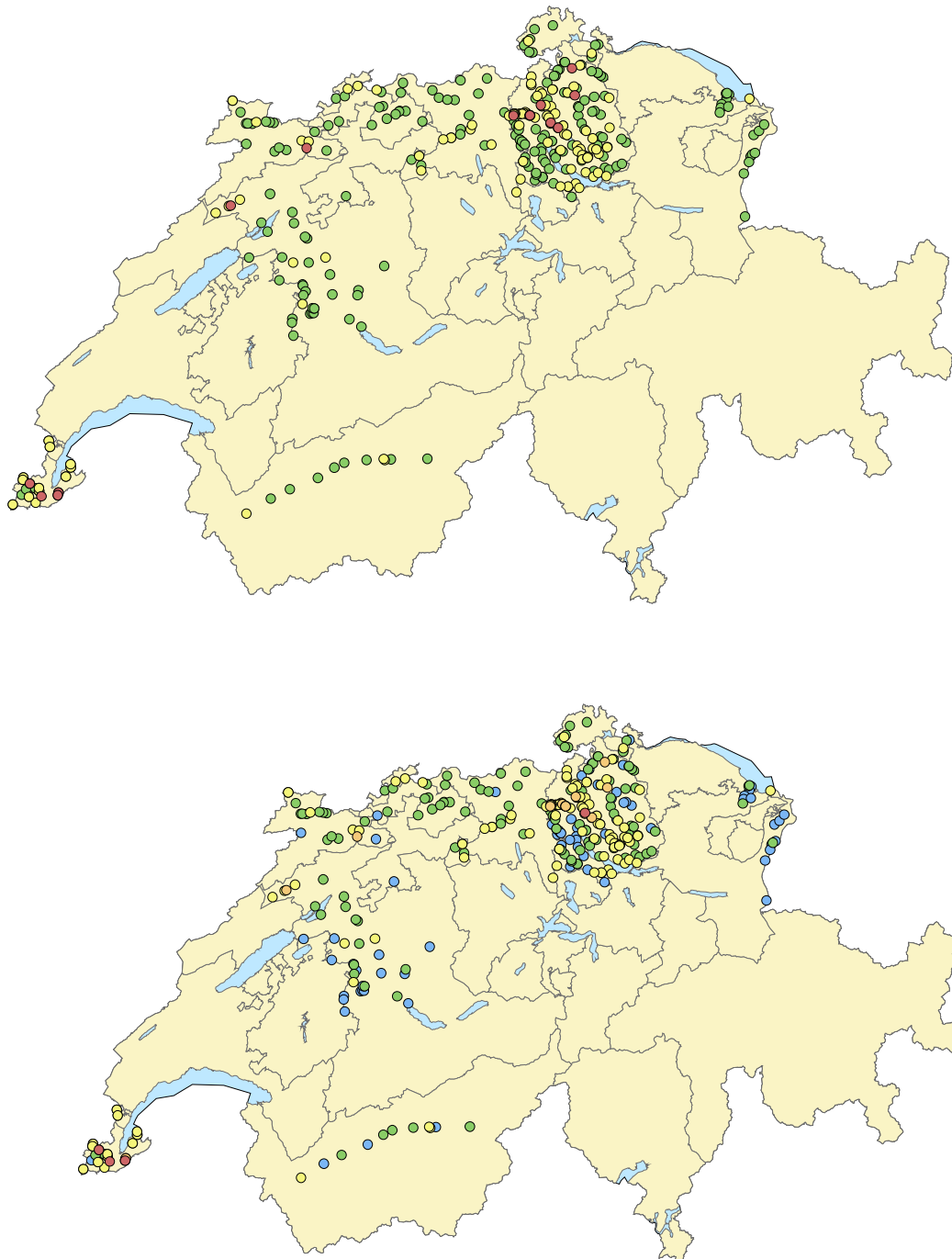


Fig. 8: Lead concentrations measured in Swiss sediments classified in three quality categories according to the TEC and PEC (above) and in five categories as explained in Table 1 (below). Source of graphic layer: Swisstopo. Data property: cantons (N=357).

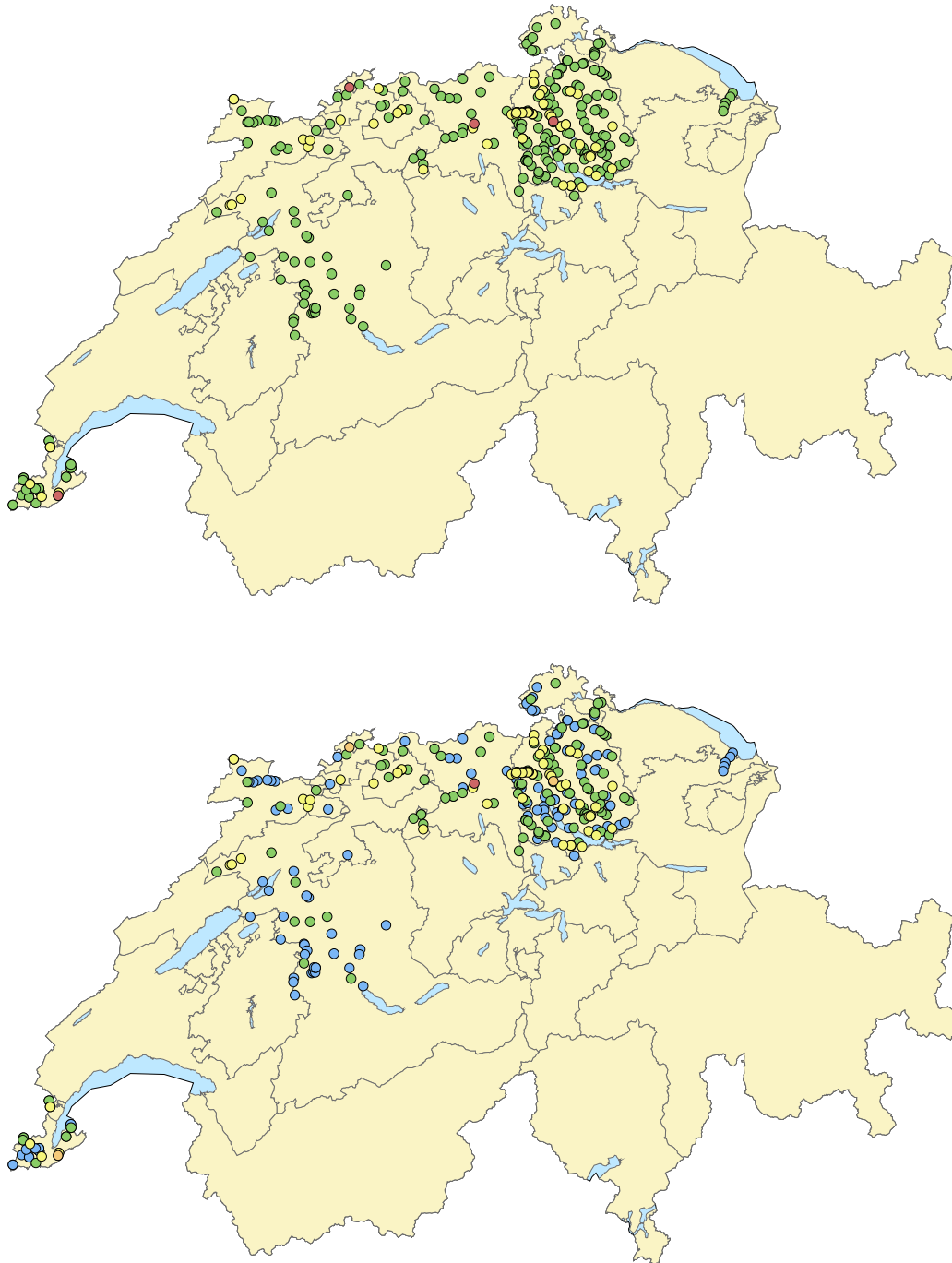


Fig. 9: Mercury concentrations measured in Swiss sediments classified in three quality categories according to the TEC and PEC (above) and in five categories as explained in Table 1 (below). Source of graphic layer: Swisstopo. Data property: cantons (N=335).

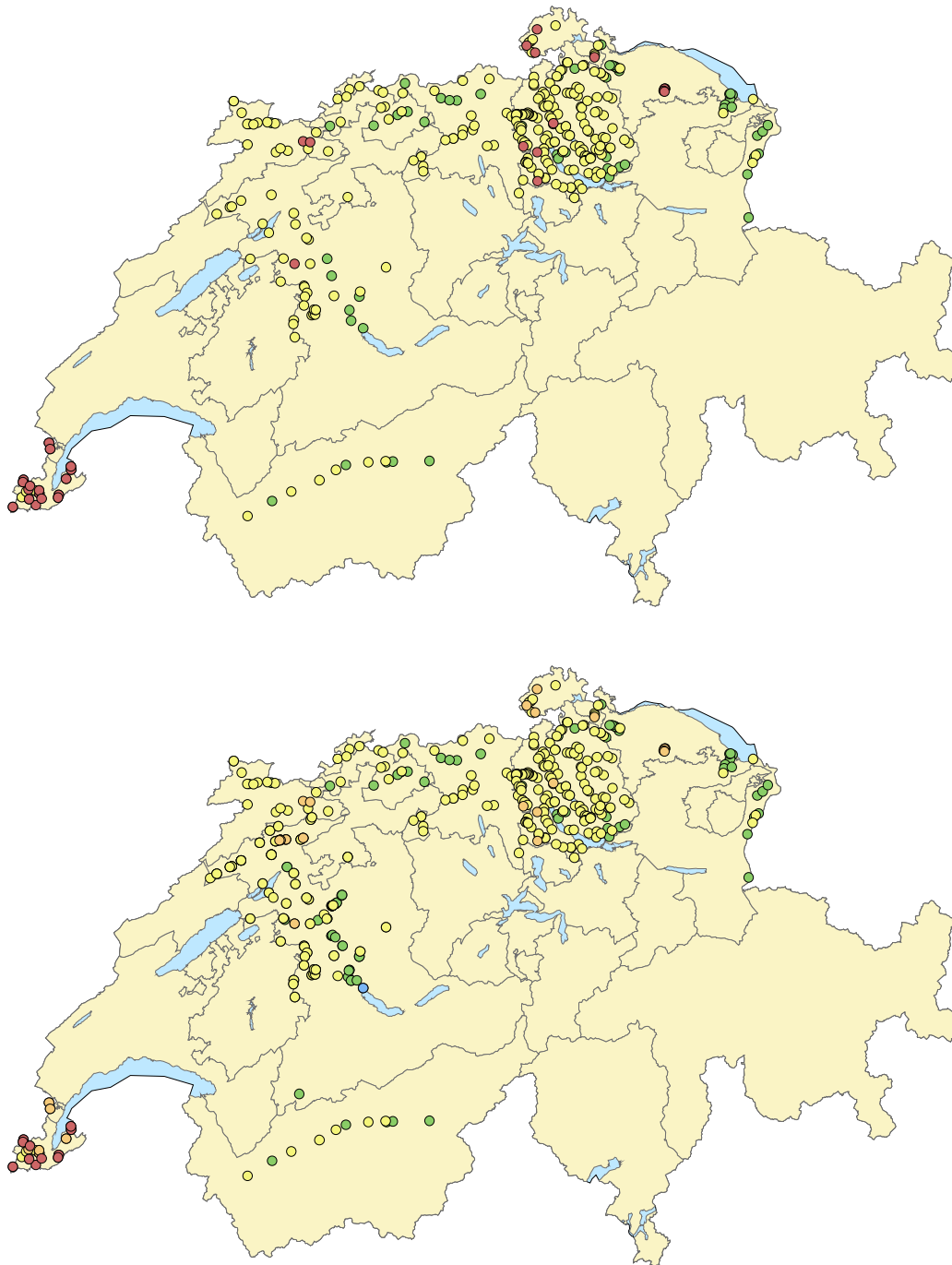


Fig. 10: Nickel concentrations measured in Swiss sediments classified in three quality categories according to the TEC and PEC (above) and in five categories as explained in Table 1 (below). Source of graphic layer: Swisstopo. Data property: cantons (N=371).

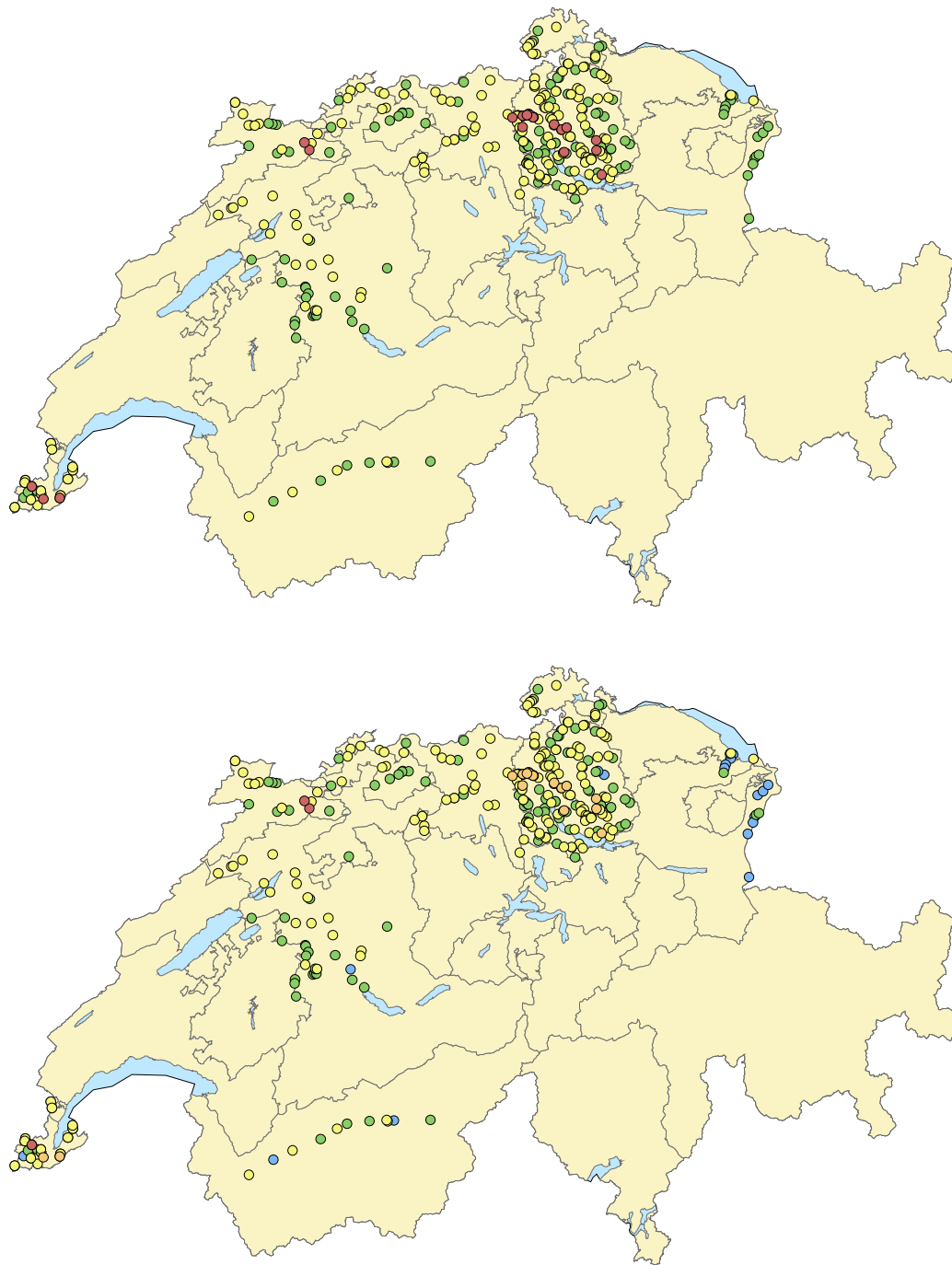


Fig. 11: Zinc concentrations measured in Swiss sediments classified in three quality categories according to the TEC and PEC (above) and in five categories as explained in Table 1 (below). Source of graphic layer: Swisstopo. Data property: cantons (N=358).

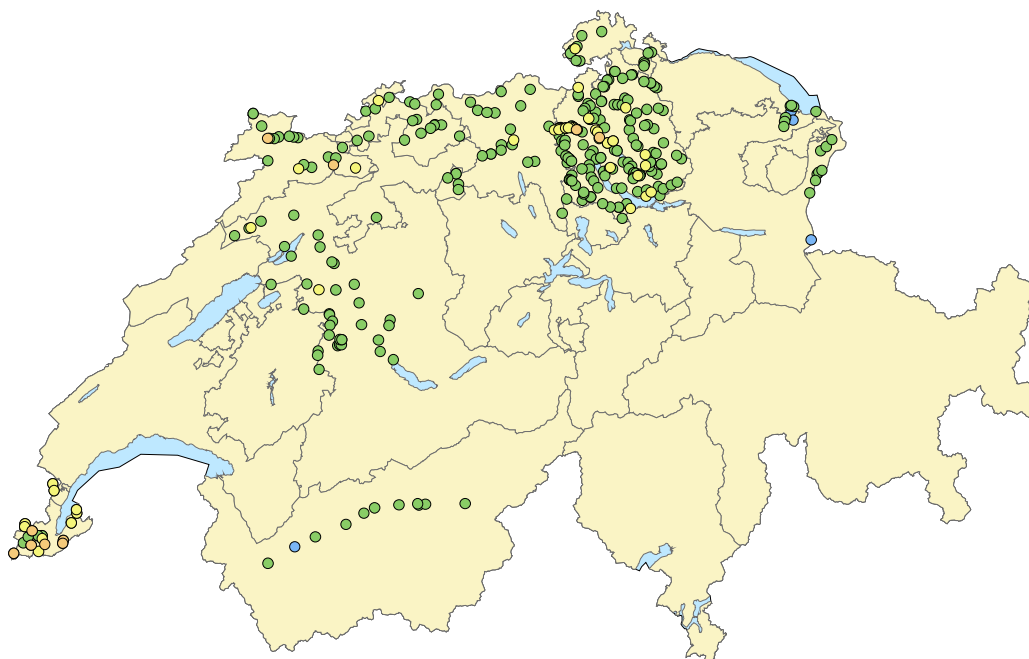


Fig. 12: Sediment contamination according to the m-PEC-Q values calculated using the measured concentrations of the metals Cd, Cr, Cu, Hg, Ni, Pb and Zn and the quality criteria developed by Ingersoll et al. (2001) (see text for details). Source of graphic layer: Swisstopo. Data property: cantons (N=358).

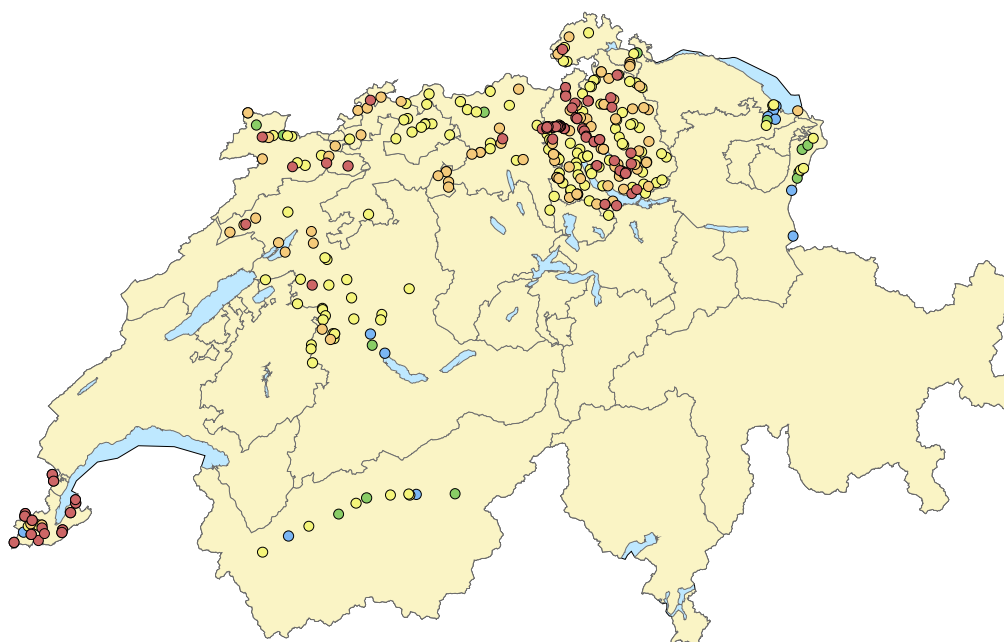


Fig. 13: Sediment contamination according to the mean PEC quotient and the quality criteria based on the oligochaete index IOBS developed by Vivien et al. (2011) (see Table 1). Source of graphic layer: Swisstopo. Data property: cantons (N=358).

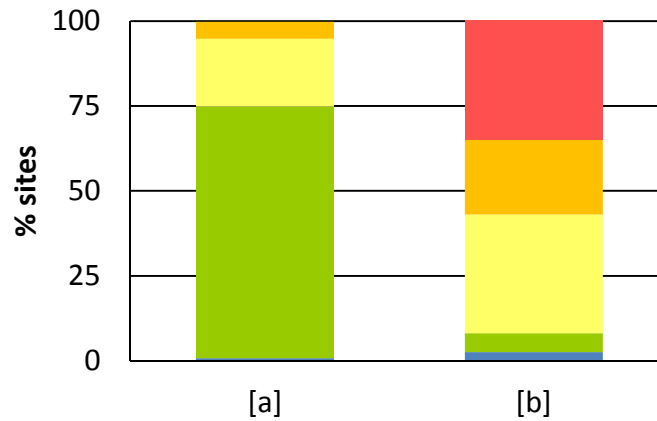


Fig. 14: Comparison of the proportion of samples classified in each of the five quality classes for each of the classification criteria: classes of *m-PEC-q* developed according to the incidence of toxicity in the amphipod toxicity test (a); classes of *m-PEC-q* developed according to the incidence of oligochaete community alteration (b).

3.6 Temporal trends

Only 10 % of the data cover entries for different years of sampling at the same sampling location and almost all of these cases correspond to two consecutive campaigns. This prevents any statistical analysis for assessing temporal trends at the same site and for the same metal. Nevertheless, we produced plots of measured sediment concentrations over time for the metals considered using all the available data (Fig. 15). These plots show a decreasing trend for all metals, suggesting an overall improvement of sediment quality in Switzerland after 1990 in terms of metal contamination. However, the concentrations do not correspond to a real temporal monitoring program and this overall decreasing trend could be just associated with different types of sites under assessment in the studies carried out at different years.

Canton Zurich performed a large sampling campaign in 1999, where sediment metal concentrations were quantified at ca. 50 sampling points distributed over the whole canton. Metal concentrations at the same location have been quantified in a subsequent campaign starting from 2002, allowing for some temporal trend analysis on sediment contamination within this canton. Tab. 5 summarises the distribution of data of concentrations in the initial campaign in 1999 and the distribution of data in the following campaigns. In order to highlight temporal trends in contamination, we have treated all data obtained from subsequent sampling campaigns as a single group, so that the statistical descriptors can be directly compared between the initial assessment and the subsequent ones.

We observe a decrease in all statistics (mean, median, and 10th and 90th percentiles) over time for the metals Cr, Ni and Pb. For these three metals, and also for Hg, a progressive downshift in the classification of samples is observed (Fig. 16). There is a decrease in the number of samples classified into the highest priority category associated with a decrease in the 90th percentile and maximum concentrations. However, the minimum, 10th percentile, median and mean experience an increase with time. For Cu, whereas the 90th percentile decreases slightly, an increase is observed for all other statistics, with the median increasing from 47.6 mg/kg in 1999 to 60.9 mg/kg and an increasing number of samples falling in the intermediate quality class.

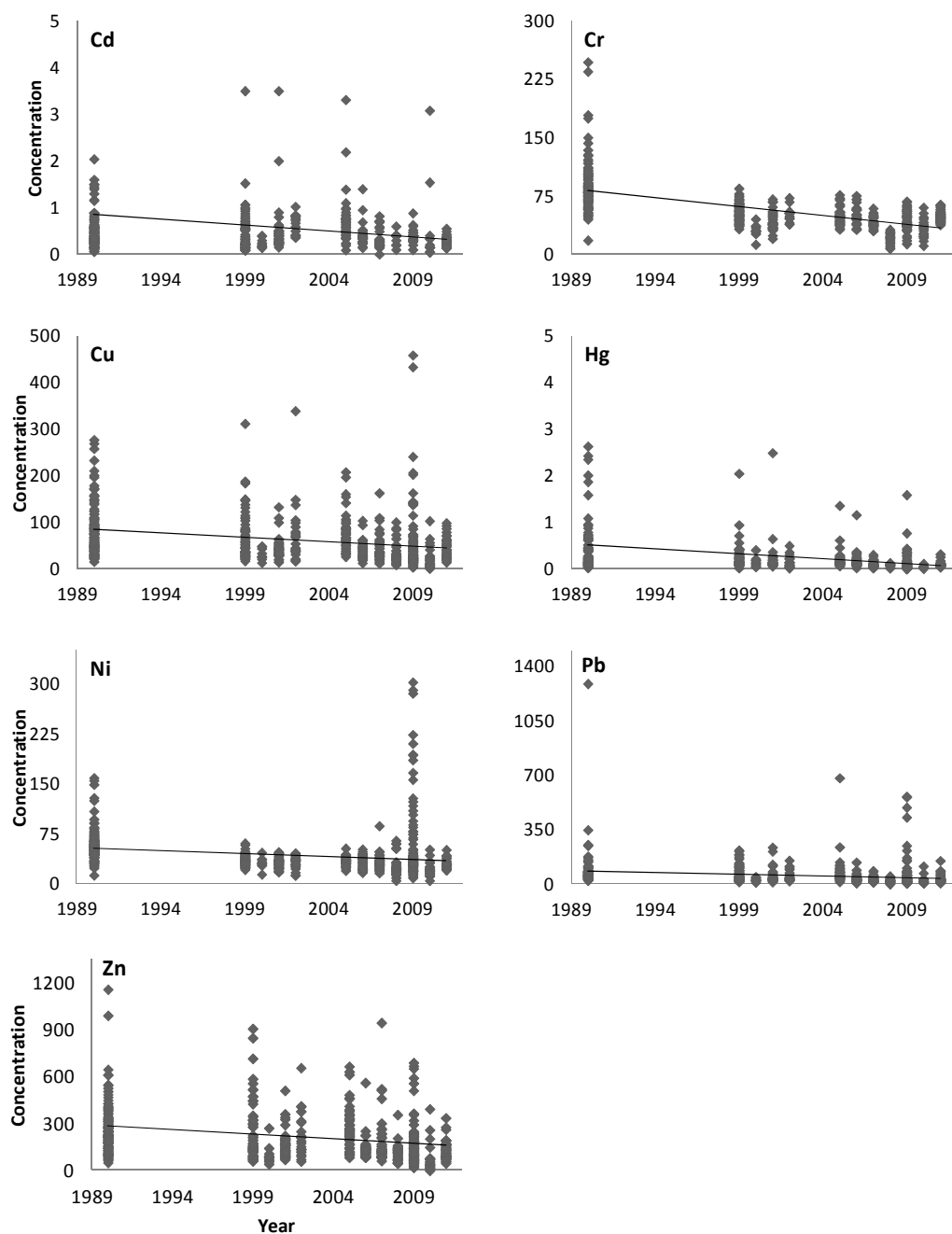


Fig. 15: Distribution of data of measured concentrations in Switzerland with time for the different metals considered. Concentrations are expressed as mg/kg dw.



Tab. 5: Statistics of data in canton Zurich. The data are separated into two groups according to the sampling date: a 1st sampling campaign performed in 1999, and the measured metal concentrations at the same location but in a subsequent campaign (from 2002 to 2011).

	Campaign	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Mean	1 st	0.5	53.7	61.0	0.2	36.1	63.1	225
	2 nd	0.6	49.6	65.3	0.2	33.2	52.0	232
Median	1 st	0.32	51.8	47.6	0.17	34.9	44.0	156
	2 nd	0.43	48.6	60.9	0.13	34.1	41.3	188
Maximum	1 st	3.5	84.6	184	2.0	61.1	190	846
	2 nd	3.3	72.2	197	0.6	51.0	237	612
Minimum	1 st	0.09	32.6	17.6	0.07	21.5	15.3	60.3
	2 nd	0.19	30.4	21.7	0.06	20.0	13.0	81.0
10 %	1 st	0.13	38.8	26.6	0.09	25.5	23.5	86.9
	2 nd	0.25	37.0	26.9	0.08	24.6	16.8	89.3
90 %	1 st	0.85	65.7	113	0.38	46.2	116	451
	2 nd	0.92	65.2	105	0.24	42.3	92.8	409

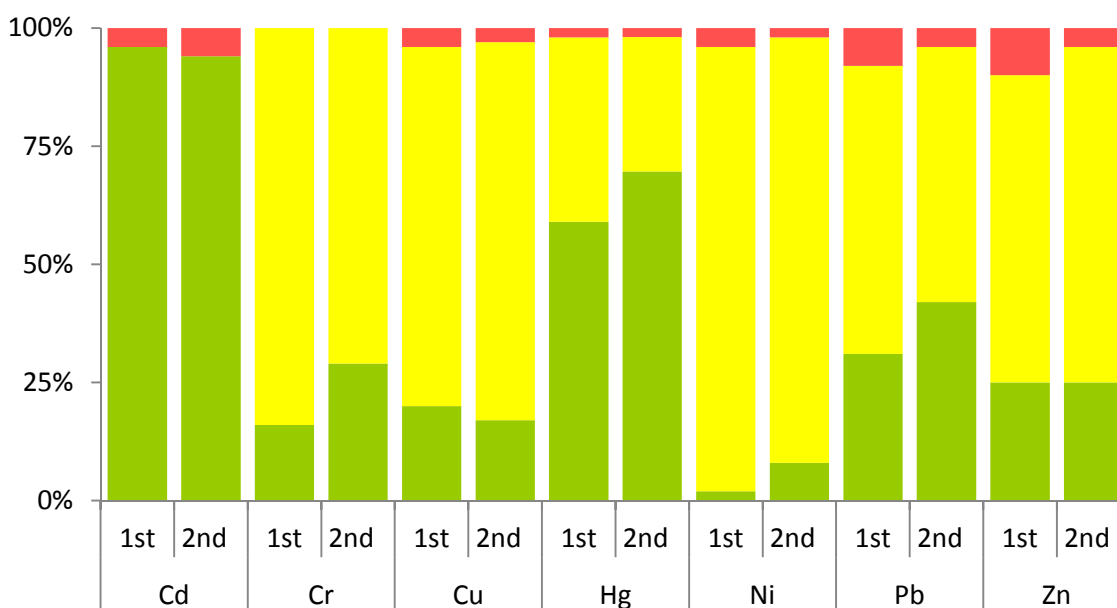


Fig. 16: Percentage of samples classified in each of the three quality criteria according to TEC-PEC values (see Table 1). The data are separated into two groups according to the sampling date: a 1st sampling campaign performed in 1999, and the measured metal concentrations at the same location but in subsequent campaigns (from 2002 to 2011).

3.7 Natural background concentrations of metals

Data on background concentrations in sediments from different types of water bodies in Switzerland were searched in the scientific literature. Whereas data on ambient levels of metal concentrations could be obtained from statistical studies, no statistical studies have been done to determine natural levels of metal concentrations in Swiss sediments.



3.7.1 Natural concentrations

The resulting data of natural levels of concentrations came mainly from lakes, where studies have addressed historical contamination in sediment cores (Tab. 7). In cores, the background values were considered those measured in the layer dated ca. 1850. Note that these concentrations refer mostly to total concentrations (extraction using hydrofluoric acid (HF) or perchloric acid (HClO₄)) and very few refer to total extractable metal concentrations (after extraction with aqua regia or nitric acid (HNO₃) without dissolving the silica matrix). Total extractable concentrations are considered a better proxy for metal bioavailability than total concentrations, thus total background natural concentrations will give no indication of risk. Rather, they intend help identifying locations that are contaminated relative to natural or ambient levels and where further work is necessary.

The variability of the data of natural concentrations in lakes expressed as the ratio between the maximum/minimum natural concentrations extends from 2 to 10 fold, with the highest ratios for Cd and Hg because of the low measured environmental concentrations. A number of factors contribute to this variability, among others the small number of cores per lake and the use of different extraction procedures. This same level of variability is found in the measured concentrations from a given sampling site at a given Swiss river in consecutive seasonal campaigns over a period of 1 year (Pardos et al. 2003). With this level of variability and often few or single data points per location, it is not possible to identify areas with specific geochemical characteristics.

3.7.2 Ambient concentrations

The ambient concentrations in stream sediments reported for Switzerland in the atlas of the Forum of the European Geological Surveys (FOREGS) are also considered. The FOREGS concentrations were calculated as the average of samples collected at 10 random sites in Switzerland (www.gsf.fi/publ/foregsatlas). These concentrations refer to the < 0.150 mm fraction after extraction with aqua regia. Other ambient levels from large datasets from Switzerland are also included. The data refer mostly to total extractable metal concentrations in the fine fractions of the sediments, although this information is not available for all data.

In general, the range of natural concentrations measured in dated cores from the different Swiss lakes are in good agreement with ambient levels of metals in Swiss sediments (Tab. 8). This includes: the median values for metals in suspended matter and sediments from large Swiss rivers established by Pardos et al (2003); the background concentrations for suspended matter used to develop the target values for sediments in the Rhine (OFEFP 1995); and the reference concentrations for the Lemanic basin (Arbouille et al. 1989; Favarger et al. 1990). However, for the determination of ambient levels in Swiss sediments, the 5th percentile of the data of the large data base from canton Bern or that from this study seems more pertinent in order to minimise the effect of point source contamination and diffuse enrichment, a factor that cannot be ruled out in studies such as the one by Pardos et al (2003)².

The FOREGS baseline concentrations for Swiss streams also fall in the low-medium range of the natural background concentrations from lake cores and the lowest range of measured concentrations in Swiss streams (see

² Data from clean streams together with the 10th percentile of all monitoring data for dissolved metal has been proposed for the derivation of background concentrations of metals in the Netherlands to be used when assessing monitoring results against the Environmental Quality Standards but using 250000 data (ten Hulscher 2013).



Tab. 8). The exception is Ni, for which natural concentrations for lakes are higher than the reference environmental concentrations for river and stream sediments, and Pb, with FOREGS baseline concentration being above the range of natural concentrations in lakes.

3.7.3 Geological contribution

Tab. 6 also includes metal concentrations in upper continental crust and average shale. Due to the heterogeneity of natural inputs, a traditional approach for the determination of natural background concentrations is to use average shale as an indicator of geological contribution to metal concentrations in sediments. The range of natural and ambient concentrations in Swiss sediments are comparable to average upper continental crust and average shale concentrations, although average shale concentrations of Cr and Ni are persistently higher than the range of natural and ambient concentrations in Swiss sediments.

3.7.4 Relevance of SQGs compared to natural background

The threshold established for the consideration of environmental concentrations as relevant for the development of threshold effect concentrations (TECs) was established by McDonald et al. (2000) in effect concentrations of at least 2-fold above the background. This criterion is also mentioned in the section related to the use of field or mesocosm data for the development of environmental quality standards for sediments in the EU Technical Guidance Document (EU 2011).

The comparison of available data for natural background concentrations in Switzerland with this threshold again identifies an issue for the metals Ni and Cr (Tab. 6, 8).

Tab. 6: Range of natural and ambient metal concentrations in Swiss sediments, compared to metal concentrations in upper continental crust (as reported in Taylor and McLennan, 2009) and average shale (as reported by Salomons and Förstner, 1984). The 5th percentile of metal concentrations in Swiss sediments and the threshold effect concentration (TEC) are included for comparison purposes. All concentrations are expressed in mg/kg dry weight.

Metal	Natural concentrations in lakes	Ambient concentrations	Upper continental crust	Average shale	5% percentile Swiss sediments database	TEC
Cd	0.1-0.5	0.14-0.5	0.098	0.22	0.14	0.99
Cr	25-50	18-80	83	90	23.2	43.4
Cu	15-50	13-50	25	45	13.1	31.6
Hg	0.02-0.2	0.03-0.2	-	0.18	0.03	0.18
Ni	40-84	14-50	44	68	17.0	22.7
Pb	10-50	11-50	17	20	11.2	35.8
Zn	40-100	51-100	71	95	51.1	121



Tab. 7: Metal concentrations measured in sediment cores from different lakes in Switzerland. All concentrations expressed in mg/kg dry weight, and refer to total sediment.

Site	Date	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Reference	Comments
Zürichsee	ca. 1800	<0.2	--	22	0.2	--	10	50	Von Gunten et al. 1997	One core, one site HNO ₃ /HClO ₄ /HF extraction
Vierwald- städtersee(Lake Lucerne)	ca. 1700 ^a	0.5	--	30	--	--	40	100	Spadini et al. 2003	One core, one site HNO ₃ /H ₂ O ₂ extraction
Lake Lucerne	ca. 1850	--	--	--	0.03	--	22	--	Thevenon et al. 2011	HNO ₃ /HClO ₄ /HF extraction
Lake Constance	pre-1900 ^b	0.1	50	28	0.1	84	10	58	Müller et al. 1997	One core, one site
Lake Constance	ca. 5000y ^c	0.1	39	34	0.05	48	20	53	Wessels 2006	Average of data from 3 to 7 m depth
Greifensee	ca. 1928	--	--	15	--	--	15	40	Imboden et al. 1980	Values determined from graph
Lake Zug	ca. 1800	--	--	--	--	--	16	--	Moor et al. 1996	Twelve cores in a transect, background determined from 1 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	HNO ₃ /HClO ₄ /HF extraction
Cadagno	pre-1850	0.4	40	50	--	40	20	100	Birch et al. 1996	HNO ₃ extraction

^a Exponential increase from 1800 to 1850.

^b Average of samples from pre-1900 (24-40 cm).

^c Average of samples from 3 to 7 m depth.



Tab. 8: Metal concentrations measured in different water bodies in Switzerland. All concentrations expressed in mg/kg dry weight.

Site	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Reference	Comments
FOREGS	--	24.8	15.3	0.037	22.1	48.0	76.1	FOREGS, 2010	Geochemical baseline, 10 random sites Measured in <0.150 mm
Swiss sediments	0.17	31.5	18.9	0.05	20.9	14.6	64.7	This report	Ca. 600 data, 10%-quartile
Swiss large rivers	0.24	32.3	34.0	0.14	32.6	26.7	101	Pardos et al., 2003	Median of 80 data of sediments and suspended matter
Lake Léman	0.2	70	30	0.03	50	30	60	Arbouille et al., 1989	Reference concentrations, no info on development
Swiss rivers, Lemanic basin	0.3	70	50	0.05	--	50	80	Faverger et al., 1990	Reference concentrations, from ca. 400 data
Bielersee	0.5	30	30	0.1	25	15	100	R. Ryser, personal communication	1947-2005, lowest values
Different streams, canton Bern	0.4	20	18	0.1	19	13	67	R. Ryser, personal communication	2003-2010, 10%-quartile
Rhin	0.3	80	20	0.2	30	25	100	OFEFP, 1995	Reference concentrations for suspended matter ^a . Measured in < 20 µm fraction
TEC	0.99	43.4	31.6	0.18	22.7	35.8	121	MacDonald et al., 2000	
PEC	5	111	149	1	49	128	460	MacDonald et al., 2000	

^a Used in the development of target values for sediments. Target values describe the limit for the first quality class. The limit for relevant sediment contamination has been fixed to the fourfold target value. The (pragmatic) definition of this criterion partly also takes into account national criteria of assessment (ICPR, 2009).

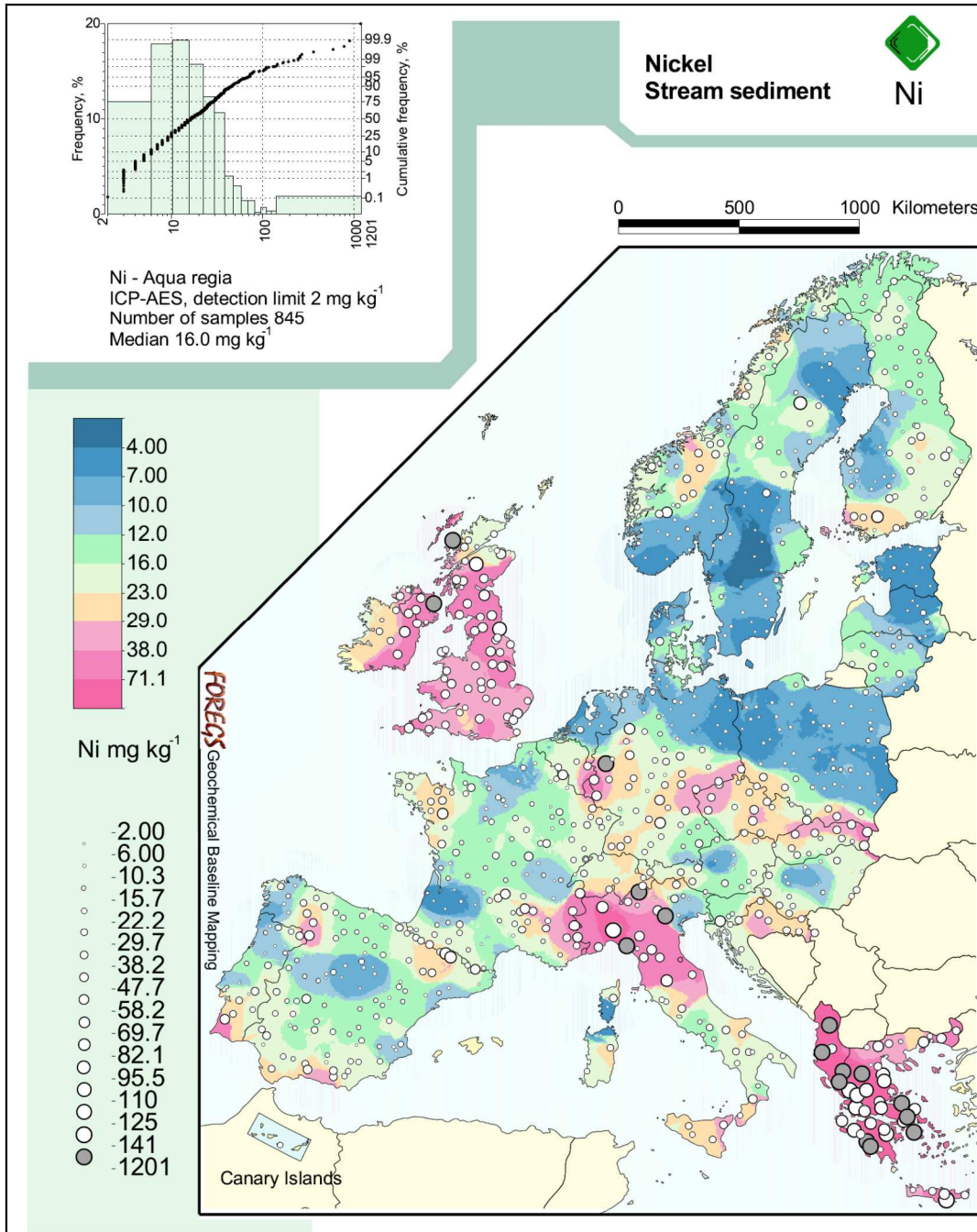


Fig. 17: Map of background Ni concentrations in stream sediments (from www.gsf.fi/publ/foregsat-las). The circles represent the measured concentrations at the sampling points used to develop the map of background concentrations. Concentrations are measured in the fraction < 0.150 after extraction with aqua regia.



4 Conclusions

The following conclusions can be drawn from the assessment of the dataset on metal concentrations in sediments:

- There is still an important area of Switzerland for which no data on sediment concentrations are available and, in most of the areas where data are available, proper monitoring programs are not set in place.
- Trace elements are classified into four separate groups according to the exceedance of probable effect concentrations (PEC): Cd, with only 1% of data above the PEC; Hg and Cr, with 3% of data above the PEC; Cu, Pb and Zn with 6% and Ni with 20% of the data above the PEC. Alternatively, frequency of exceedance of other sets of quality guidelines can be used for the prioritisation of metals in Swiss sediments (e.g. the order of metals according to the percentage of exceedance of the ICPR target value is Cu (40%) > Zn (33%) > Ni (19%) > Pb (11) > Hg (6%) > Cd (5%)). The intended uses and development method of the SQGs entail some differences that should be considered for interpretation of the results.
- Five categories are proposed for each single metal using factors of TEC-PEC values, but these interpretation criteria should only be considered an effective communication tool or, at most, to identify potential reference sites.
- The most problematic metal identified so far is Ni, which is present at medium-high concentrations in the majority of samples. It is likely that these high concentrations are associated with a relatively high natural concentration of Ni in Swiss sediments rather than anthropogenic sources of pollution.
- With the small database available and its patchy distribution within the Swiss area, it is currently not possible to identify geographical trends within Switzerland in terms of geochemical properties to define their corresponding background or baseline concentrations with confidence.
- The available data on natural background concentrations of Ni (and to a lesser extent of Cr) are above the 2-fold threshold established for assessing the relevance of effect concentrations for the development of TEC. The TECs for these two metals should be used with care.
- The general trends over the last decade indicate a decrease in the sediment metal concentrations across the regions that have been considered so far, with a progressive downshift in the classification of samples to lower priority categories.

5 Recommendations

- The establishment of a monitoring program that targets sediment quality with respect to a list of priority contaminants, in line with the National River Monitoring and Survey Program (NADUF) and the Swiss Soil Monitoring Network (NABO), would allow mapping sediment quality over the whole Swiss area, and assessing whether sediment quality is improving at contaminated sites according to environmental protection measures.
- In order to obtain homogeneous and comparable data sets, and to maximize the benefits derived from their interpretation, a common approach for sampling, pre-treatment and analysis should be adopted on a pan-national level. The current development of the module “sediment” takes this aspect into account.
- The use of TEC-PEC values is a good approach to identify samples with concentrations of low concern and those of high concern for the metals considered in terms of their



potential ecotoxicological properties. The exception is Ni and to a lesser extent Cr, for which relatively high background concentrations in some areas may lead to an overestimation of risk. The use of TEC-PEC should only be considered provisionally until sediment quality criteria have been derived for Switzerland or a proper validation for its use in Switzerland is completed.

- A tiered approach that includes an initial comparison against TEC-PEC values and a subsequent consideration of background/natural metal concentrations for sites exceeding the threshold for effects can provide the degree of flexibility until any set of sediment quality criteria are validated in Switzerland.
- A more comprehensive data base should be developed before metal background concentrations can be applied with confidence in sediment quality assessment. Given the likely variability in geology, reference concentrations on a river basin scale should be used when they are available. The FOREGS maps can be used for improving the interpretation of measured metal concentrations together with sediment quality criteria such as the corresponding TEC-PEC values.
- Mean quotients can be used to integrate the overall contamination at a site into a single value. Such a chemical index can be useful for an effective communication of prioritisation of sites through the use of a single value or colour. The type of data used for the development of quality classes for ranges of mean quotients in terms of chemicals and biological/ecotoxicological effect considered should be kept in mind.

6 References

- Alloway BJ. 1990. Heavy metals in soils. Glasgow: Blackie and Son.
- Arbouille D, Howa H, Span D, Vernet JP. 1988. Etude général de la pollution par les métaux et répartition des nutriments dans les sédiments du Léman. Campagne 1988. Commission Internationale pour la Protection des Eaux du Léman contre la Pollution, Lausanne.
- Bay SM, Ritter KJ, Vidal-Dorsch DE, Field LJ. 2012. Comparison of national and regional sediment quality guidelines for classifying sediment toxicity in California. *Integrated Environmental Assessment and Management* 8, 597-609.
- Birch L, Hanselmann KW, Bachofen R. 1996. Heavy metal conservation in Lake Cadagno sediments: historical records of anthropogenic emissions in a meromictic alpine lake. *Water Research* 30: 679-687.
- European Commission. 2011. Common implementation strategy for the Water Framework Directive (2000/60/EC). Technical Guidance for Deriving Environmental Quality Standards. Guidance document No. 27. Technical Report doi: 10.2779/43816.
- Faverger PY, Span D, Vernet JP. 1990. Métaux lourds dans les sédiments des rivières du bassin Lémanique suisse. Commission Internationale pour la Protection des Eaux du Léman contre la Pollution, Lausanne.
- Field LJ, Norton SB. 2014. Regional models for sediment toxicity assessment. *Environmental Toxicology and Chemistry* 33, 708-717.
- Flück R, Chèvre N, Campiche S. 2011. Surveillance de la qualité des sédiments en Suisse : Synthèse d'un questionnaire. Septembre 2011, Centre Ecotox, Lausanne, Suisse. Available at: http://www.oekotoxzentrum.ch/dokumentation/berichte/doc/Sedimentsynthese_FR.pdf
- Flück R, Campiche S, de Alencastro LF, Ferrari BJD, Rossi L, Santiago S, Werner I, Chèvre N. 2012. Surveillance de la qualité des sédiments. État actuel des méthodes disponibles et mise en place de recommandations. *Aqua & Gas* 4. Avril 2012.



- Flück R, Chèvre N, Campiche S. 2012. Surveillance de la qualité des sédiments en Suisse. Etat actuel des méthodes disponibles et mise en place de recommandations. Rapport final Septembre 2012, Centre Ecotox, Lausanne, Suisse. Available at: http://www.oekotoxzentrum.ch/dokumentation/berichte/doc/Sedimente_final_FR.pdf
- Hou A, DeLaune RD, Tan MH, Reams M, Laws E. 2009. Toxic elements in aquatic sediments: distinguishing natural variability from anthropogenic effects. *Water, Air and Soil Pollution* 203, 179–191.
- International Commission for the Protection of the Rhine (ICPR) 2009. Sediment management plan, Rhine. Report n° 175, Koblenz, Germany.
- International Commission for the Protection of the Rhine (ICPR). 2007. Comparaison de l'état du Rhin de 1990 à 2004. Rapport N° 164 Kaiserin-Augusta-Angalen 15, D 56068 Coblenz.
- Imboden DM, Tschopp J, Stumm W. 1980. Die Rekonstruktion früherer Stofffrachten in einem See mittels Sedimentuntersuchungen. *Schweizerische Zeitschrift für Hydrologie-Swiss Journal of Hydrology* 42, 1-14.
- Ingersoll CG, MacDonald DD, Wang N, Crane JL, Field LJ, Haverland PS, Kemble NE, Lindskoog RA, Severn C, Smorong DE. 2001. Predictions of sediment toxicity using consensus-based freshwater sediment quality guidelines. *Archives in Environmental Contamination and Toxicology* 41, 8-21.
- Lamy F, Guex B, Keimer C, Boivin P. 2014. Réseau d'observation des sols genevois (GEOS). Bilan de trois campagnes de suivi.
- MacDonald DD, Ingersoll CG, Berger T. 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Archives in Environmental Contamination and Toxicology* 39, 20-31.
- Moor CH, Schaller T, Sturm M. 1996. Recent Changes in Stable Lead Isotope Ratios in Sediments of Lake Zug, Switzerland. *Environmental Science and Technology* 30, 2928-2933.
- Müller G, Grimmer G, Böhnke H. 1977. Sedimentary record of heavy metals and polycyclic aromatic hydrocarbons in Lake Constance. *Naturwissenschaften* 64, 427-431.
- Office Fédéral de la Protection de l'Environnement (OFEV). 1998a. Ordonnance du 28 octobre 1998 sur la protection des eaux (OEaux). No. RS 814.201. Berne, Suisse.
- Office Fédéral de l'environnement (OFEV). 1998b. Ordonnance du 1er juillet 1998 sur les atteintes portées aux sols (OSol). N° RS 814.12. Berne, Suisse.
- Office Fédéral de l'Environnement, des Forêts et du Paysage (OFEFP). 1995. Métaux dans les sédiments. Cahier de l'Environnement n° 240, protection des eaux, Berne, Suisse.
- Pardos M, Houriet JP, Dominik J. 2003. Micropolluants dans les sédiments. Métaux et micropolluants organiques dans les matières en suspension et sédiments superficiels des grands cours d'eau suisses. Cahiers de l'environnement. Office Fédéral de l'Environnement, des Forêts et du Paysage, Berne. No. 353.
- Salminen R (Chief-editor), Batista MJ, Bidovec M, Demetriades A, De Vivo B, De Vos W, Duris M, Gilucis A, Gregorauskiene V, Halamic J, Heitzmann P, Lima A, Jordan G, Klaver G, Klein P, Lis J, Locutura J, Marsina K, Mazreku A, O'Connor PJ, Olsson SÅ, Ottesen RT, Petersell V, Plant JA, Reeder S, Salpeteur I, Sandström H, Siewers U, Steenfelt A, Tarvainen T. 2005. *Geochemical Atlas of Europe. Part 1: Background Information, Methodology and Maps*. Espoo, Geological Survey of Finland, 526 pages, 36 figures, 362 maps.
- Salomon W, Förstner U. 1984. *Metals in hydrocycle* Berlin: Springer.
- Schmid P, Holm P, Brüscheweiler B, Kuchen A, Staub E, Tremp J. 2010. Polychlorobiphényles (PCB) dans les eaux en Suisse. Données concernant la contamination des poissons et des eaux par les PCB et les dioxines: évaluation de la situation. Office féd., Berne: Office fédéral de l'environnement (OFEV).



- Spadini L, Sturm M, Wehrli B, Bott M. 2003. Analysis and dating of Pb, Cd, Cu, Zn sediment profiles from the Vitznau basin of Lake Lucerne (Switzerland). *Revue de Géographie alpine* 1, 41-48.
- Taylor SR, McLennan SM. 2009. *Planetary Crusts: Their Composition and Evolution*. Cambridge University Press, Cambridge. 378 pp.
- ten Hulscher D. 2013. Deriving background concentrations for metals. Multilateral meeting, January 2013.
- Thevenon F, Guédron S, Chiaradia M, Loizeau JL, Poté J. 2011. Pre-historic changes in natural and anthropogenic heavy metals deposition inferred from two contrasting Swiss Alpine lakes. *Quaternary Science Reviews* 30, 224-233.
- Vivien R, Lafont M, Perfetta J. 2011. Proposition d'un seuil de toxicité des métaux lourds des sédiments mis en évidence par les vers oligochètes dans quelques cours d'eau. *Bull. Soc. Vaud. Sc. Nat.* 92.
- VonGunten HR, Sturm M, Moser RN. 1997. 200-year record of metals in lake sediments and natural background concentrations. *Environmental Science and Technology* 31, 2993-2997.
- Wenning RJ, Batley GE, Ingersoll CG, Moore DW (Ed.). 2005. *Use of sediment quality guidelines and related tools for the assessment of contaminated sediments*. Pensacola (FL): Society of Environmental Toxicology and Chemistry (SETAC). 815 p.
- Wessels M. 2006. *Bodensee-Untersuchung-Seeboden*. Abschlußbericht für die Projektträger Internationale Gewässerschutzkommission für den Bodensee und Interreg IIIA Alpenrhein - Bodensee – Hochrhein.



7 Indices

7.1 List of Figures

Fig. 1: Distribution of metal concentrations measured in Swiss sediments. The reference values used to classify concentrations according to different criteria are included for comparison purposes. See text for details.	8
Fig. 2: Component scores for the seven variables.	9
Fig. 3: Factor loadings for the cases included in the initial PCA (a) and when excluding the cases with conspicuous metal concentrations (b).	10
Fig. 4: Correlation plot of nickel versus chromium concentrations in Swiss sediments (solid line) and average concentrations in rocks (dotted line).	10
Fig. 5: Cadmium concentrations measured in Swiss sediments classified according to the TEC and PEC in three quality categories (above) and in five categories (below). Categories are explained in Table 1. Source of graphic layer: Swisstopo. Data property: cantons (N=305).	14
Fig. 6: Copper concentrations measured in Swiss sediments classified in three quality categories according to the TEC and PEC (above) and in five categories as explained in Table 1 (below). Source of graphic layer: Swisstopo. Data property: cantons (N=358).	15
Fig. 7: Chromium concentrations measured in Swiss sediments classified in three quality categories according to the TEC and PEC (above) and in five categories as explained in Table 1 (below). Source of graphic layer: Swisstopo. Data property: cantons (N=298).	16
Fig. 8: Lead concentrations measured in Swiss sediments classified in three quality categories according to the TEC and PEC (above) and in five categories as explained in Table 1 (below). Source of graphic layer: Swisstopo. Data property: cantons (N=357).	17
Fig. 9: Mercury concentrations measured in Swiss sediments classified in three quality categories according to the TEC and PEC (above) and in five categories as explained in Table 1 (below). Source of graphic layer: Swisstopo. Data property: cantons (N=335).	18
Fig. 10: Nickel concentrations measured in Swiss sediments classified in three quality categories according to the TEC and PEC (above) and in five categories as explained in Table 1 (below). Source of graphic layer: Swisstopo. Data property: cantons (N=371).	19
Fig. 11: Zinc concentrations measured in Swiss sediments classified in three quality categories according to the TEC and PEC (above) and in five categories as explained in Table 1 (below). Source of graphic layer: Swisstopo. Data property: cantons (N=358).	20
Fig. 12: Sediment contamination according to the m-PEC-Q values calculated using the measured concentrations of the metals Cd, Cr, Cu, Hg, Ni, Pb and Zn and the quality criteria developed by Ingersoll et al. (2001) (see text for details). Source of graphic layer: Swisstopo. Data property: cantons (N=358).	21
Fig. 13: Sediment contamination according to the mean PEC quotient and the quality criteria based on the oligochaete index IOBS developed by Vivien et al. (2011) (see Table 1). Source of graphic layer: Swisstopo. Data property: cantons (N=358).	21
Fig. 14: Comparison of the proportion of samples classified in each of the five quality classes for each of the classification criteria: classes of m-PEC-q developed according to the incidence of toxicity in the amphipod toxicity test (a); classes of m-PEC- q developed according to the incidence of oligochaete community alteration (b).	22
Fig. 15: Distribution of data of measured concentrations in Switzerland with time for the different metals considered. Concentrations are expressed as mg/kg dw.	23
Fig. 16: Percentage of samples classified in each of the three quality criteria according to TEC-PEC values (see Table 1). The data are separated into two groups according to the sampling date: a 1 st sampling campaign performed in 1999, and the measured metal concentrations at the same location but in subsequent campaigns (from 2002 to 2011).	24
Fig. 17: Map of background Ni concentrations in stream sediments (from www.gsf.fi/publ/foregsatlas). The circles represent the measured concentrations at the sampling points used to develop the map of background concentrations. Concentrations are measured in the fraction < 0.150 after extraction with aqua regia.	29



7.2 List of Tables

Tab. 1: Different criteria used for the classification of samples into quality classes. C: measured concentration of each metal; TEC/PEC: threshold and probable effect concentrations for each metal; m-PEC-q: mean quotient calculated using PEC values; m-TEC-q: mean quotient calculated using TEC values. See text for detailed explanation.	3
Tab. 2: Sediment fraction and extraction method used prior to quantification of metal concentration in sediments.....	6
Tab. 3: Descriptive statistics of sediment metal concentrations in the dataset. All data expressed as mg/kg dry weight. C means measured concentration. LOD is method detection limit. Values higher than TEC are underlined, and those higher than PEC are bold.....	7
Tab. 4: Classification of samples according to the m-PEC-Q values calculated using the measured concentrations of the metals Cd, Cr, Cu, Hg, Ni, Pb and Zn. Classification into classes follows results from Ingersoll et al. (2001).....	13
Tab. 5: Statistics of data in canton Zurich. The data are separated into two groups according to the sampling date: a 1 st sampling campaign performed in 1999, and the measured metal concentrations at the same location but in a subsequent campaign (from 2002 to 2011).	24
Tab. 6: Range of natural and ambient metal concentrations in Swiss sediments, compared to metal concentrations in upper continental crust (as reported in Taylor and McLennan, 2009) and average shale (as reported by Salomons and Förstner, 1984). The 5 th percentile of metal concentrations in Swiss sediments and the threshold effect concentration (TEC) are included for comparison purposes. All concentrations are expressed in mg/kg dry weight.	26
Tab. 7: Metal concentrations measured in sediment cores from different lakes in Switzerland. All concentrations expressed in mg/kg dry weight, and refer to total sediment.	27
Tab. 8: Metal concentrations measured in different water bodies in Switzerland. All concentrations expressed in mg/kg dry weight.	28