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EnviTox – Quality Control of the First Fieldwork and Sampling Stage

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EnviTox – Quality Control of the First Fieldwork and Sampling Stage</td></tr>
<tr><td colspan="4">Abstract
The EnviTox project has carried out the first fieldwork and sampling phase to get information for the studies of the environmental status and potential impacts of the toxic waste landfill as well as illegal landfills and waste storage within the surrounding of Krasny Bor. Altogether 122 soil samples, 22 stream sediment samples, 22 surface water samples as well as 5 groundwater samples were taken from the project study area and analysed for several elements and compounds. The fieldwork and sampling took place in August 2019. Seven surface water samples were taken as monitoring samples in October 2019 as well.
The quality assurance consisted of 18 control samples, the sampling staff training and the preparation of the Sampling Guidelines. The Sampling Guidelines include the field manual and the sampling plan as well as the detailed instructions for the fieldwork, the sampling of surface water, groundwater, stream sediment, soil and snow and recommendations for the sampling equipment.
The training, the guidance for sampling and the meetings ensured that the sampling staff was well prepared for the sampling. Some of the sampling equipment was not totally accordant with the recommendations. The number of the quality control samples is according to recommendations. The analysis methods used for soil and sediment samples differ remarkably from the Finnish practices of metal analyses. Thus, the metal concentrations in soil and sediment samples are not comparable to the Finnish guideline values nor the GTK results of the project standard or geochemical mappings. While the lead and mercury concentrations in the surface water blank sample were high, the lead and mercury concentrations in the surface water samples should be considered only suggestive. More information about the Russian analysis methods for organic compounds is needed to ensure the comparability of the results to the Finnish guideline values. Some suggestions to improve the sampling and analysis methods used in the next sampling phases are given.</td></tr>
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1. Introduction

The environmental impacts of the Krasny Bor toxic waste landfill (EnviTox) -project is a co-operative project between the State Geological Unitary Company «Mineral» (SC Mineral), the Institute of Limnology, Russian Academy of Sciences (IL RAS), the Geological Survey of Finland (GTK) and the South-Eastern Finland University of Applied Sciences (Xamk). The project is co-funded by the South-East Finland – Russia Cross-border Cooperation Programme (CBC Programme 2014-2020) supporting EU's external actions with the financing from the European Union, the Russian Federation and the Republic of Finland.

The EnviTox project is aiming at developing feasible recommendations and tools for ensuring good quality environment in the Krasny Bor toxic waste landfill surroundings. The project will provide up-to-date information on the state of the environment in the area around the Krasny Bor toxic waste landfill and suggest feasible measures for its improvement. Based on the vulnerability and risk analysis, feasible risk management measures for improving the status of the environment are given. Implementation of these measures will lead to improvement of the environmental status in the region.

The toxic waste landfill Krasny Bor occupies 73 hectares and it is located about 30 kilometres to the south-east of the city of St. Petersburg. From 1969, altogether 2 million tons of toxic waste was accumulated into 70 ponds excavated in the Cambrian clay. The thickness of the clay layer is several tens of meters. Five of the ponds are not remediated yet and they contain about 700 000 m^3 of toxic liquid waste. The landfill stopped accepting toxic waste in 2014 and since 2016, the measures to eliminate the accumulated environmental damage have been carried out. These works are planned to be completed by the end of 2025. In addition, large amounts of toxic waste both from the landfill itself and from illegal waste storages have been accumulated in the surrounding area. The main part of the environmental activities is concentrated on the territory of landfill and its sanitary protection zone. Environmental assessment outside this area has not systematically been provided. The Baltic Marine Environment Protection Commission (HELCOM) has identified the Krasny Bor toxic waste landfill as a major hot spot of the Baltic Sea Region from 1993 to the present. In addition, both in the east and west side of the Krasny Bor toxic waste landfill, there are plenty of industrial activities which may affect the environmental condition as well.

The EnviTox study area locates between Izhora and Tosna rivers and its size is 65 km^2. The EnviTox project plan for the fieldwork and sampling that support environmental impact assessment is divided into three stages. At the first stage, the samples of different natural matrices like surface water and groundwater, stream sediments and soil samples are taken. The aim of the analysis results of these samples is to get an overall picture of the environmental status in the Krasny Bor toxic waste landfill surroundings. In addition, the first fieldwork and sampling stage helps to detect the illegal landfills and the toxic waste disposal sites that exist in the study area. In order to find out the possible impact of atmospheric deposition from the landfill, snow samples will be taken at the second stage. The third stage will concentrate in more detailed studies of selected sites to support the environmental risk assessment.

In addition to three individual sampling stages, surface water monitoring is established during the first sampling stage. The monitoring of surface water quality is needed to obtain relevant information about the possible discharges of contaminated wastewater from the landfill and other possible pollution sources into the river network surrounding the study area. The monitoring is planned to contain automatic online monitoring as well as regular sampling of surface water. The automatic monitoring will be carried out at a site of discharge of treated surface water from the landfill. The regular surface water sampling is targeted to several checkpoints of the river network.

The chemical analyses of the samples contain inorganic elements, several organic compounds and pesticides. For water samples, the common indicators characterizing the water and potential pollution have been determined. The analytical studies are conducted in the Russian laboratories with a mandatory analytical audit in the accredited laboratories.

Quality control is essential in order to ensure that the obtained data are fit for purpose. Quality control shall cover all aspects of work from the start (field sampling) to the finish (laboratory analysis). In this quality control report, the quality assurance process of the first sampling stage in the EnviTox project is discussed. The main focus is on the results of the quality control samples of different matrices used in the first sampling round as well as on the practices of the analytical laboratory. In addition, attention has been paid to sampling practices.

2. Quality assurance

The main aim of the sampling is to provide information for the study questions. The risk analysis and all the conclusions depend on the contaminant concentrations analysed from the samples. Thus, all the samples as well as sampling and analysis methods are chosen to support the objectives of the study. The main aim in taking samples for the chemical analyses is to have a sample which represents the study area and the studied matrix as good as possible. The reliable and representative sampling is based on a comprehensive sampling plan. It is recommended that the sampling personnel is accomplished and experienced in sampling, preferably certified to take the samples. The sampling methods have to be relevant and all the equipment that is used in the sampling should be suitable for the purpose, clean and inert. The storage and transport of samples should be appropriate and not affecting the samples. The quality assurance and the safety matters should be agreed in advance and taken into account throughout the project.

The quality assurance contains of all the operations which are used to ensure that the received results fit the agreed demands. The uncertainty of the sampling is identified, measured and controlled with quality assurance samples. To ensure a good quality geochemical sampling, the sampling personnel should be trained. In Finland, it is recommended that sampling personnel has relevant knowledge and certificates for sampling (http://www.syke.fi/fi-FI/Palvelut_aineistot/Ymparistonaytteenottajien_henkilosertifiointipalvelu) and previous experience in geochemical sampling.

In general, it is recommended to take duplicate samples at least 5 % of the total number of the samples to ensure the quality of sampling. This applies to all different sampling matrices included in the study. The field duplicate samples are taken the same way as the routine samples (Salminen et al. 1998). The quality of water sampling is ensured with blank samples (0-samples). The blank samples are prepared from deionized (distilled) water the same way as the routine samples. In the Geological Survey of Finland (GTK), the practice in geochemical water sampling is to take one blank sample in each sample batch although the number of samples is less than 20.

The laboratories that are used for analysis should preferably have the accreditation, and their analytical methods should have the accreditation or they should be based on standards. It is important to pay attention to the detection limits and the limits of quantification of the elements to be determined. Accredited testing laboratories enforce their own customary quality assurance methods.

2.1 The planned quality assurance in the EnviTox project

In order to ensure qualitative sampling with uniform methods, a training for the personal attending the sampling is fundamental. Xamk is authorized by the Finnish Environment Institute to give certified sampling training in Finland in the area of soil and solid waste sampling and water sampling and measurement. Thus, it was agreed that sampling training will be organized by Xamk in Mikkeli for the EnviTox working group.

In the EnviTox project, general guidance for sampling was gathered in the EnviTox – Guidelines for Sampling, Analysis and Quality Assurance -report (Hatakka et al., 2019). The detailed instructions for the fieldwork and the sampling of surface water, groundwater, stream sediment and soil as well as snow, and the sampling equipment are given in Appendix 1 of the report. The sampling plan and field manual were established and agreed by the project team, and finalized by the coordinator. The EnviTox sampling plan is presented in Appendix 2 of the report. For the sampling stages 2 and 3, the sampling plan presented in Appendix 2 will be updated if needed. The sampling plan is planned to be delivered and presented beforehand to each person who attends to the sampling. Before the sampling, all the people who are responsible or taking part in the sampling are planned to be gathered together in a meeting where the sampling plan is gone through carefully. This is to ensure that all the sampling staff is, in addition to the practical and technical issues, aware of the purpose of the sampling as well as the safety issues, and reports sampling in a consistent manner.

In the first fieldwork and sampling stage of the EnviTox project, the sample network for soil was planned using the systematic grid. For sediment, surface and groundwater samples, the sampling network was based on the random and judgemental sampling models while the locations of rivers, streams and ditches are not evenly distributed. It was known that the logistics in the study area is sometimes challenging and thus the network for soil sample locations became more random than systematic as well.

In the first sampling stage, the soil and sediment samples were agreed to be taken according to the Russian standards (GOST 17.4.4.02-2017, GOST 17.4.3.01-2017, Guidelines for the assessment of air pollution by their content in the snow cover and soil 1990). The use of these standards was justified to ensure that the results are comparable with other similar studies carried out especially in the Krasny Bor area but generally in Russia as well. It is also essential that the results are comparable with national reference values. The soil samples were agreed to be taken from a depth of 0–5 and 5–20 cm "by envelope" in the square of 50 m x 50 m as composite samples. The composite soil sample is made by mixing at least five sub-samples. The number of sub-samples for a composite sediment sample depends on the property of the stream bed: as many sub-samples are taken from the river bed along the stream as there is enough sample material for the analyses. All the water samples in the EnviTox project were planned to be taken as single samples. It was agreed that the decision of the sample types at the third sampling stage will be made after the interpretation of the first and second fieldwork and sampling stage results.

According to the Sampling Guidelines, all the sampling equipment as well as all the sample bottles and bags should be clean and inert. If sampling equipment are used in several sampling sites e.g. water pumps, spades for digging and measuring instruments, they have to be cleaned or disinfected between the separate sampling points. The cleaning agent must be selected so that it itself does not cause any contamination of the samples, usually distilled and deionized or infusion water and colourless paper towels are used. Quality control procedures were established to confirm that cleaning procedures are adequate. It was recommended that the sampling procedure with water sampling equipment as well as the sample bottles are checked in a test sampling where e.g. from a couple of sampling sites the samples are taken and analysed before the actual sampling session.

The identification of the samples, the sample IDs, have to be unambiguous and clear. The sample IDs used in the EnviTox project were given in the Sampling Guidelines. The IDs have to be marked in all sampling-wares carefully e.g. with permanent drawing ink and/or with adhesive labels. It was recommended to check that the IDs do not wear away during the transportation and storage and it was recommended to use an extra sample ID in a small plastic bag which was meant to be included in the plastic bag where e.g. all the water sample bottles or soil and sediment bags of a sampling site are gathered.

According to the Sampling Guidelines, after the sampling, the samples for metal analyses were recommended to be preserved with acid based on the methods agreed with the laboratory. The samples were recommended to be taken in a laboratory as soon as possible. In practice, it is not conceivable to transport the samples directly to the laboratory after the sampling, but the storage time should be kept as short as possible. During the storage, the conditions of samples (temperature and light) are kept as close to their origin as possible, e.g. protected from direct light and excessive heat. To avoid cross contamination in the storage space the sample containers (bags, bottles) have to be tightly sealed and isolated from sample containers of other matrices in being. All the samples should have been packed carefully to prevent breakage of the bottles and bags during the storage and transportation.

The content of the sample identification sheets was agreed between the project partners for each sample media. In the EnviTox project, there are sample sheets for every sampling matrix (Sampling Guidelines, Appendices 3 – 9). The sampling sheets were filled in in connection of the sampling and the sampling sites were photographed according to the instructions given in the Sampling Guidelines. The sampling personnel was expected to report the sampling and field measurement as well as the possible departures from practice and methods during the sampling to the coordinator as well as to the fieldwork and sampling report. All the field observations as well as the results of laboratory analyses were inserted into a database and gathered in excel files delivered to all project partners.

According to the Sampling Guidelines several quality assurance samples were planned to be taken. The quality assurance samples for soils were a project standard sample, a reference sample near the Krasny Bor area, field duplicate samples and laboratory replicate samples. In addition, comparison of analysis results of soil samples between Russian and Finnish laboratories was planned to be performed. For the stream sediment samples, the quality assurance samples were planned to be field duplicate and laboratory replicate samples. For water samples, the quality were planned to be assured with blank samples, field duplicate samples and replicate samples. The laboratory carrying out measurements of field duplicate samples twice are considered as replicate samples. In addition, accredited testing laboratories enforce their own customary quality assurance methods.

According to the Sampling Guidelines, the samples as well as sampling and analyses methods are chosen to support the objectives of the study. The laboratories responsible of the analyses and the analysing methods were chosen and agreed by SC Mineral. In the working group meeting in Mikkeli in June 2019, it was discussed that the soil and sediment samples will be analysed using strong HNO_3 leach. In the working group meeting in St. Petersburg in August 2019, the partners were informed that the soil and sediment analyses will be carried out of < 1 mm fraction size material. The water sample analyses at the first sampling stage were discussed during the Sampling Guideline writing process. It was decided to analyse the total element concentrations in water samples while the Russian guideline values were told to base on these and the earlier Krasny Bor studies had used this method as well.

2.2 The realization of the quality assurance at the first sampling stage

In the EnviTox project, all the personal attending the sampling gathered together in Mikkeli and had a training for soil, surface water, sediment and groundwater sampling by the approved trainers of Xamk in June 10th – 13th, 2019. The training consisted selected parts of Finnish certified sampling training and included the basic theory for sampling, quality assurance and safety issues as well as practical training for soil and water sampling and for field measurements. All the attendees received a testimony on their participation in the course. In the EnviTox working group meeting beyond the training, the sampling plan for the first sampling phase of the EnviTox project was created and agreed (Hatakka et al., 2019).

The manuscript of the EnviTox Sampling Guidelines was finished before the first fieldwork and sampling stage took place. Only some minor points in the manuscript were to be checked in parallel with fieldwork and sampling.

The whole sampling team, including attendees from GTK and Xamk, gathered in St. Petersburg in August 12th, 2019 for a working group meeting to discuss and agree on the sampling plan, the guidelines and some other sampling details and practices. The sampling of water, sediment and soil samples had started in the Krasny Bor study area already in August 5th, 2019. The whole project team participated in the sampling session during August 13th – 15th, 2019. In a working group meeting in August 16th, 2019, the sampling practices and all the feedback by sampling personnel were concluded.

The training, the guidance for sampling and the meetings ensured that the sampling staff was well prepared for the sampling. Some of the sampling equipment was not totally accordant with the recommendations. For example, the bottles for the metal analysis of water samples had the preservation acid inside the bottle and the bottles were closed with a black cap. The coloured cap while being in contact with the preservation acid might cause some contamination to the sample. The sampling buckets of water samples were colourful as well. There was some confusion about the soil sample material in relation to the sampling depths in the beginning. However, this was discussed and clarified in the working group meeting in St. Petersburg in August 16th, 2019.

At the first sampling phase of the EnviTox project, five duplicate samples at the depth of 0 – 5 cm and five duplicate samples at the depth of 5 – 20 cm were taken for the quality assurance of soil sampling. The amount of the duplicate samples is 8.2 % of the total number of each sampling depth and thus, their amount is adequate if compared with the recommendations. In addition, two GTK soil reference samples were used as project standards and sent to the laboratory analysis together with the soil samples. The GTK soil reference sample is prepared of dried and homogenized soil material from the Pirkanmaa region in Finland. This reference sample material is used regularly in GTK's geochemical soil studies as a project standard and it is attached to all soil sample batches sent to laboratory analysis. The reference sample is always analysed with the same methods as the routine samples. In the EnviTox project, selected inorganic elements were analysed from the project standard. The laboratory which was used for the analysis of the EnviTox first sampling stage made the double measurements of pH, As, Cd, Cr, Hg, Zn and benzo(a)pyrene for the routine and duplicate samples. These results are handled as replicate samples in the EnviTox project quality assurance process. The planned reference soil sample near the Krasny Bor area for the dioxin analysis was not taken.

For the stream sediment sample batch, two field duplicate samples were taken. The amount of the duplicate samples is 9.1 % of the total number of stream sediment samples and thus, in comparison to the recommendations, the amount is adequate.

For the surface water sample batch, two field duplicate samples and one blank sample were taken. The amount of the duplicate samples is 9.1 % which follows the recommendations. One blank sample is 4.5 % of the total amount of the surface water samples which is slightly below the recommendations. In total, 43 element and compound concentrations and water properties were analysed of the blank sample. The blank sample was taken during the actual sampling session. Thus, the recommendation of the test sampling before actual sampling was not followed.

Some of the surface water sampling sites sampled during the first sampling phase were included in the surface water monitoring. In October 2019, when the second sampling round of the surface water monitoring took place, no blank or field duplicate samples were taken. Thus, the quality assurance recommendations were not followed.

For the groundwater sample batch, one blank sample was taken. This is 20 % of the total groundwater sample amount and thus in line with the recommendation to have one blank sample in a batch. Only 14 metal analyses were carried out of the blank sample. No duplicate groundwater samples were taken. The blank sample was taken during the actual sampling session. Thus, the recommendation of the test sampling before actual sampling did not take place.

According to the project plan, the description of the fieldwork and the sampling process should be presented in the fieldwork report, and according to the Sampling Guidelines, the deviations from the sampling instructions and sampling plan should be reported. The fieldwork description as well as the situation of the deviations during the sampling session are not reported in the 1st fieldwork report. Thus, the 1st fieldwork report is partly insufficient and does not serve the quality assurance process. One confusion in the sample IDs was detected in the original laboratory analysis report but evidently it has been solved by SC Mineral.

The laboratories responsible for the analyses of the samples and the sampling methods were chosen by SC Mineral. Some differences between analyses methods used in Russian and Finland were found. The analysis methods are described more detailed in Chapter 3.

3. Comparison of Russian and Finnish analysis methods

3.1. Inorganic elements

In the 1st fieldwork and sampling phase, the analyses of soil and sediment samples were carried out from the < 1 mm grain size fraction and 5M HNO_3 was used for leaching. In Finland, the Finnish reference values to assess soil and sediment contamination are based on analyses of < 2mm grain size fraction, and *aqua regia* (AR) extraction is recommended for minerogenic material and strong nitric acid (14 M HNO_3) leach for minerogenic material with a high organic matter content (humus, sludge). Thus, the extraction used in Finland is much stronger than in Russia to determine the concentrations of inorganic elements in soil and sediment, and analysis results of the first sampling phase are not comparable to the Finnish guideline values.

Water samples for cation and metal analyses were taken in a 0.25 l plastic bottle with 10 ml HNO_3 acid added into it in the laboratory beforehand (ratio 4 ml HNO_3 / 100 ml water). In Finland, the dissolved element concentrations (cation and metal) in water are analysed from the water samples which have been filtered using 0.45 µm filter and preserved with strong HNO_3 with the ratio 0.5 ml HNO_3/100 ml water. The total element (cation and metal) concentrations in Finland are analysed from untreated water samples (non-filtered) which have been preserved with 12.5 ml HNO_3 / 100 ml water. Thus, the surface water and

groundwater analysis results of the first sampling phase are not directly comparable to the Finnish guideline values.

3.2. Organic substances

In Russia, determination of organic substances are carried out taking into account the drying of the samples to an air-dry state. According to analysis methods used in Finland, field moist soil samples are used. If the sample contains particles larger than 2 mm and/or contaminant is heterogeneously distributed, the samples are pre-treated. If moderately volatile (e.g. mineral oil, PAH, PCB, organochlorine pesticides) to non-volatile organic compounds are to be measured, samples are chemically dried at a low temperature (− 196 °C, liquid nitrogen), ground and sieved (ISO 14507).

In Russia, soil and sediment samples are extracted with acetone and hexane and analysed by gas chromatography (in the case of analysis of samples for PCB and pesticides) and liquid chromatography (in the analysis of samples for benzo(a)pyrene). When analysing water samples, hexane is used as an extraction solvent for PCB. However, extraction solvents used in water analysis for other organic compounds than PCB and measurement techniques are not known at the moment. Russian method (PND F 16.1:2:2.2:3.56-08) for analysing dioxins and furans PCDD/PCDF from soil and sediment is the same as ISO 13914:2008. However, dioxin-like PCBs are not included to the analysis like in Finland.

The analysis methods used in Finland partly use different extraction solvents and measurement techniques (Table 1).

Table 1. Description of analysis methods recommended to use in Finland (Ministry of Environment 2014 and 2018) for analysing some organic compounds.

Analyte	Method	Pre-treatment	Extraction solvent	Other steps	Measurement
PAH	SFS-EN ISO 17993 (water)		liquid-liquid extraction with hexane	concentration, cleaning with silica if necessary	HPLC with fluorescence detection
	SFS-ISO 18287 (soil)	field-moist or chemically dried samples (ISO 14507:2003)	acetone and petroleum ether	washing with water, drying with anhydrous sodium sulfate, if needed: clean-up with silica and concentration	GC-MS
Polychlorinated biphenyls (PCB), organochlorine pesticides (e.g. gamma-HCH, hexachlorobenzene, heptachlor, DDD, 4,4-DDT, DDE)	SFS-EN ISO 6468:1997 (water)	normally not necessary	liquid-liquid extraction, hexane, petroleum ether or heptane	concentration, clean-up	GC + electron-capture detector (ECD)
	SFS-ISO 10382:2007 (soil)	field-moist samples or pretreatment (ISO 14507)	acetone and petroleum ether	concentration, removing polar compounds with aluminium oxide column, if needed: removing elemental sulfur with	GC + electron-capture detector (ECD)

Analyte	Method	Pre-treatment	Extraction solvent	Other steps	Measurement
				tetrabutylammonium sulfite reagent	
Σ PCDD-PCDF-PCB (WHO-TEQ)	ISO 13914: 2013 (soil)	dried, preferably freeze-dried, samples. Usually <2 mm fraction of the dry and ground or sieved solid sample.	Soxhlet extraction (with toluene) or equivalent method.	clean-up (usually multi-column liquid chromatographic techniques), concentration	gas chromatography with high-resolution mass selective detection (GC/HRMS) (isotope dilution technique)
Mineral oil: >C10-C21, >C21-C40, >C10-C40	ISO 16703 (soil)	the homogenized field-moist or pretreated soil sample (ISO 14507)	mechanical shaking or sonication with acetone/n-heptane	washing of organic layer with water, removing polar compounds by adsorption on Florisil	GC + flame ionization detection (FID)
Alkylphenols Pentachlorophenol	SFS-EN ISO 18857-1 (water)	the acidified water sample	toluene	cleaning with silica, if necessary	GC-MS
Chlorophenols: 2,3-, 2,4- 2,5-, 2,6-, 3,4- and 3,5-dichlorophenol; 2,3,4-, 2,3,5-, 2,3,6-, 2,4,5-, 2,4,6- and 3,4,5-trichlorophenol, 2,3,4,5- and 2,3,4,6-tetrachlorophenol and pentachlorophenol	SFS-ISO 14154 (soil/ sediment)		an acid-base solid/liquid extraction (acetone-hexane at low pH)	acetylation and liquid/liquid extraction (hexane)	GC + electron-capture detector
Highly volatile halogenated hydrocarbons (e.g. trichloroethylene, chloroform)	SFS-EN ISO 10301:1997 (water)	filling the bottle completely (no headspace), sodium thiosulfate to bottle prior to sampling (if reaction with organic matter)	liquid-liquid extraction with pentane (or hexane, petroleum ether, heptane, xylene)	filtering through glass wool or centrifugation	GC + electron-capture detector (or other suitable detector)

4. Recommendations for the limits of quantification of chemical analysis in Finland

The limit of detection is the concentration of the analyte, which differs significantly from blank sample (at a certain level of confidence) and indicates the presence of the analyte in the sample. The Limit of Quantification means a stated multiple of the limit of detection at a concentration of the analyte that can reasonably be determined with an acceptable level of accuracy and precision. (Ministry of the Environment 2018) In most cases, the limits of quantification are considered to be 5, 6 or 10 times the standard deviation of the blank. There is a grey area between the limit of detection and the limit of quantification in which the analyte can be reliably detected, but its quantification involves considerable uncertainty (Hiltunen et al. 2011).

Laboratory used by the EnviTox project has not given the limits of quantification for analysed parameters in the analysis reports, but the detection limits are indicated in the protocols when a result is obtained below the detection limit specified in the measurement methods. Laboratories must use the detection limits specified in the approved guidelines. In the results protocols, the detection limits are indicated by the measurement procedures, i.e. those analyte values for which accuracy and precision indicators are established in the methods. The limit of quantitative detection of analyte in the protocols issued by the laboratory is not taken into account, because when performing research and drawing up protocols, the laboratory relies only on the values metrologically established in the measurement procedures and indicated in the laboratory accreditation area.

Detection limits reported by the laboratory were compared to the Finnish recommendations for limits of quantification. However, it is important to note that the detection limit of the analysis is lower than the limit of quantification. Some differences between analysis methods used in Finland and Russia were also found and can affect the comparison of the analysed concentrations to Finnish values.

Stream water samples

According to the requirements of the Finnish Government Decree on Substances Dangerous and Harmful to the Aquatic Environment (23.11.2006/1022), Annex 3 the limit of quantification of the analytical method shall not exceed 30 % of the Environmental Quality Standard (EQS); and level of measurement uncertainty shall not exceed 50 %. SFS, EN or ISO standards or methods that are equivalent in accuracy and reliability should be used in analyses.

Detection limits of the Russian standard methods were compared to the Finnish minimum performance requirements (limit of quantification). For many contaminants (mercury, cadmium, PAH compounds, DDT, trichloroethylene and chloroform), detection limits were higher than the Finnish minimum performance requirements (Table 2). For cadmium, benzo(a)pyrene and chloroform, detection limits were even higher than the Finnish Environmental Quality Standards. Detection limits are higher than EQS given as an arithmetic annual mean for nickel and lead as well.

In Finland, EQS is set only for substances identified as dangerous and harmful for aquatic environment according to EU´s Water Framework Directive or national legislation. Therefore, comparison of detection/quantification limits in Table 2 is made only for these substances.

Table 2. Comparison of detection limits of the Russian standard methods to the quantification limits of SFS/ISO standards, the Finnish Environmental Quality Standard (EQS) values and minimum performance requirements. *Russian detection limit is higher than the Finnish minimum performance requirements (the limit of quantification). **Russian detection limit is higher than the Environmental Quality Standard in Finland.

Component	**Detection limit in Russia (mg/dm^3)**	**Limit of quantification in standard methods used in Finland (mg/dm^3)**	**EQS in Finland* (mg/dm^3)**	**Target for Limit of Quantification in Finland** (mg/dm^3)**
COD	<5			
BOD 5 days	<2			
BOD total	<2			
Ammonium (NH_4^+)	<0.01			
Nitrites (NO_2^-)	<0.01			
Nitrates (NO_3^-)	<0.01			
Sulphates (SO_4^{2-})	<2.0			
Chloride ions (Cl^-)	<10			
Fluoride ion (F^-)	<0.15			
Hydrocarbonate (HCO_3^-)	<10			
Cyanide ion	<0.005			
Evaporated residue	<50			
Suspended substances	<0.5			
Hydrogen sulphide (H_2S)	<0.002			
Sulphides (S^{2-})	<0.0019			
Formaldehyde	<0.02			
Surface active anionic substances	<0.010			
Phenols	<0.0005	SFS-EN ISO 18857-1.2007: Nonylphenol 0.000005 Octylphenol 0.000005 Pentachlorophenol 0.0001	Nonylphenol 0.0003/0.002 Octylphenol 0.0001/- Pentachlorophenol 0.0004/0.001	Nonylphenol 0.0001 Octylphenol 0.00003; 0.000003 Pentachlorophenol 0.00013
Oil products, total	<0.05			
Mercury (Hg)	**<0.00005***	**SFS-EN ISO 12338-1999: 0.00001 ISO 17582:2006: 0.00001**	**-/0.00007[4]**	**0.000016**
Chrome (Cr^{3+})	<0.01			
Chrome (Cr^{6+})	<0.01			
Cadmium (Cd)	**<0.001****	**SFS-EN ISO 17294-2:2005: 0.000005-0.001**	**≤0.00008-0.00025/ ≤0.00045-0.0009[3,4]**	**0.00003-0.0008**

Component	Detection limit in Russia (mg/dm^3)	Limit of quantification in standard methods used in Finland (mg/dm^3)	EQS in Finland* (mg/dm^3)	Target for Limit of Quantification in Finland** (mg/dm^3)
Nickel (Ni)	<0.005		0.004/0.034[4]	0.006
Lead (Pb)	<0.002		0.0012/0.014[4]	0.0022
Common Iron (Fe)	<0.01			
Manganese (Mn)	<0.001			
Copper (Cu)	<0.001			
Zinc (Zn)	<0.001			
Cobalt (Co)	<0.005			
Aluminium (Al)	<0.006			
Vanadium (V)	<0.002			
Calcium (Ca)	<0.2			
Magnesium (Mg)	<0.04			
Potassium (K)	<1.0			
Sodium (Na)	<1.0			
Benzo(a)pyrene	**<0.0005****	**SFS-EN ISO 17993: 2004: 0.00001**	**-/0.000027**	**0.000016**
4.4'-DDT	**<0.00001***	**SFS-EN ISO 6468:1997: 0.000001-0.00001[6]**	**0.000025/-**	**0,000003 (para-para-DDT) 0.000008 (total DDT[10])**
Total PCB[9]	Information not given			
Trichloroethylene	**<0.010***	**SFS-EN ISO 10301:1997 or SFS-EN ISO 15680:2004: 0.00005**	**0.01/-**	**0.003**
Chloroform	**<0.015****	**SFS-EN ISO 10301:1997: 0.00005 SFS-EN ISO 15680:2004: 0.00001**	**0.0025/-**	**0.0008**
Bromides (Br^-)	<0.05			
Total PAH icluding:	<0.04		Not applied[5]	
Napthalene	**<0.02***	**SFS-EN ISO 17993: 2004[7] (SFS-EN ISO 15680:2004): 0.00001**		**0.0008; 0.0004**
Acenaphthene	<0.006			
Fluorene	<0.006			
Phenanthrene	<0.006			
Anthracene	<0.001			

Component	Detection limit in Russia (mg/dm^3)	Limit of quantification in standard methods used in Finland (mg/dm^3)	EQS in Finland* (mg/dm^3)	Target for Limit of Quantification in Finland** (mg/dm^3)
Fluoranthene	**<0.02***	**0.00001[7]**		**0.00003**
Pyrene	<0.02			
Benzo(a)anthracene	<0.006			
Chrysene	<0.003			
Benzo(b)fluoranthene	**<0.006***	**0.00001[7]**		**0.000005**
Benzo(k)fluoranthene	**<0.001***	**0.00001[7]**		**0.000005**
Benzo(a)pyrene	**<0.001****	**0.00001[7]**	**-/0.000027**	**0.000016**
Dibenzo(a,h)anthracene	<0.006			
Benzo(q,h,i)perylene	**<0.006***	**0.00001[7.8]**		**0.0000000035**
Indeno(1,2,3-cd)pyrene	**<0.02***	**0.00001[7.8]**		**0.0000000035**
Organic carbon	<1.0			

[1] Environmental Quality Standards in inland surface water (µg/l). AA-EQS (arithmetic annual mean)/MAC-EQS (maximum allowable concentration). Government Decree on Substances Dangerous and Harmful to the Aquatic Environment 23.11.2006/1022
[2] Source: Ministry of Environment 2018
[3] EQS for cadmium and cadmium compounds varies according to hardness of water (five class for waterhardness)
[4] EQS for metals is for soluble concentration (filtered samples). Natural background concentration will be added to the EQS concentration.
[5] Benzo(a)pyrene is considered as indicator for other polyaromatic hydrocarbons.
[6] GC / ECD; In practice, the limit of quantification for total DDT (sum of four isomers) too high.
[7] Same standard for all PAHs.
[8] Enough sensitive standard method is not available.
[9] The following PCBs were analysed, which sum of them were higher than the detection limit of the method: PCB-28, PCB-29, PCB-47
[10] The total DDT is sum of 1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethane, 1,1,1 - trichloro-2- (o-chlorophenyl) -2- (p-chlorophenyl) ethane, 1,1-dichloro-2,2 bis (p chlorophenyl) ethylene, and 1,1-dichloro-2,2 bis (p-chlorophenyl) ethane

Groundwater samples

In Finland, the limit of quantification of the analytical method used must not exceed 30 % of the maximum value of the variable/substance. (Decree of Ministry of Social Affairs and Health 17.11.2015/1352)

Detection limits of the Russian standard methods were compared to recommended limits of quantification in Finland (Table 3). For cobalt, trichloroethylene and total PAH, the detection limits of the Russian standard methods were higher than the Finnish recommendations for limits or quantification. The comparison was made only for the analysed substances/variables listed in the Finnish Decree of Ministry of Social Affairs and Health 17.11.2015/1352.

Table 3. Comparison of detection limits of the Russian standard methods for groundwater analysis to the recommended limits of quantification for drinking water samples in Finland. *Detection limit of the Russian standard method is higher than recommended limit of quantification in Finland.

Component	Method of research	Units	Detection limit in Russia	Target limit of quantification in Finland[1]
Odor	РД 52.24.496-2018	points		
Colour	ПНД Ф 14.1:2:4.207-04	degree		
Turbidity	ПНД Ф 14.1:2:3:4.213-05	mg/dm3	<0.58	
Total hardness	РД 52.24.395-2017	degree		
Permanganate oxidation	ПНД Ф 14.1:2:4.154-99	mgO/dm^3		
Alkalinity	ГОСТ 31957-2012	mmol/dm^3		
Ammonium (NH_4^+)	РД 52.24.383-2018	mg/dm^3	<0.01	0.15
Nitrites (NO_2^-)	РД 52.24.381-2017	mg/dm^3	<0.01	0.15
Nitrates (NO_3^-)	РД 52.24.380-2017	mg/dm^3		15
Sulphates (SO_4^{2-})	ПНД Ф 14.1:2.159-2000	mg/dm^3		75
Chloride ions (Cl^-)	РД 52.24.407-2017	mg/dm^3	<10.0	75
Fluoride ion (F^-)	ПНД Ф 14.1:2:4.270-2012	mg/dm^3	<0.15	0.45
Hydrocarbonate (HCO_3^-)	ПНД Ф 14.1:2:3.99-97	mg/dm^3		
Evaporated residue	ПНД Ф 14.1:2:4.114-97	mg/dm^3		
Hydrogen sulphide (H_2S)	РД 52.24.450-2010	mg/dm^3	<0.002	
Sulphides (S^{2-})	РД 52.24.368-2006	mg/dm^3	<0.0019	
Surface active anionic substances		mg/dm^3	<0.01	
Phenols	ПНД Ф 14.1:2:4.182-2002	mg/dm^3	<0.0005	
Oil products	ФР 1.31.2011.11315	mg/dm^3	<0.04	
Mercury (Hg)	ПНДФ 14.1:2:4.160-2000	mg/dm^3	<0.00005	0.0003
Chrome (Cr^{3+})	ПНД Ф 14.1:2:4.52-96	mg/dm^3	<0.01	
Chrome (Cr^{6+})		mg/dm^3	<0.01	
Cadmium (Cd)	М-03-505-119-08	mg/dm^3	<0.0005	0.0015
Nickel (Ni)		mg/dm^3	<0.002	0.006
Lead (Pb)		mg/dm^3	<0.005	0.003
Common Iron (Fe)		mg/dm^3	<0.05	0.06
Manganese (Mn)		mg/dm^3	<0.005	0.015
Copper (Cu)		mg/dm^3	<0.001	0.6
Zinc (Zn)		mg/dm^3	<0.005	
Cobalt (Co)		mg/dm^3	**<0.005***	0.0006
Aluminium (Al)		mg/dm^3	<0.01	0.06
Vanadium (V)	РД 52.24.377-2008	mg/dm^3	<0.002	
Calcium (Ca)	ПНД Ф 14.1:2:4.137-98	mg/dm^3	<0.2	
Magnesium (Mg)		mg/dm^3	<0.04	
Potassium (K)	ПНД Ф 14.1:2:4.138-98	mg/dm^3	<1.0	
Sodium (Na)		mg/dm^3	<1.0	60
Benzo(a)pyrene	ПНД Ф 14.1:2:4.186-02	µg/dm^3	<0.0005	0.003

Component	Method of research	Units	Detection limit in Russia	Target limit of quantification in Finland[1]
4,4´-DDT	ПНД Ф 14.1:2:3:4.204-04	mg/dm^3	<0.00001	
Total PCB[2]		mg/dm^3		
Trichloroethylene	РД 52.24.482-2012	mg/dm^3	**<0.010***	0.003
Bromides (Br^-)	ПНД Ф 14.2:4.176-2000	mg/dm^3	<0.05	
Total PAH including:	ПНД Ф 14.1:2:4.70-96	µg/dm^3	**<0.04***	0.03
Naphthalene		µg/dm^3	<0.02	
Acenaphthene		µg/dm^3	<0.006	
Fluorene		µg/dm^3	<0.006	
Phenanthrene		µg/dm^3	0.009	
Anthracene		µg/dm^3	<0.001	
Fluoranthene		µg/dm^3	<0.02	
Pyrene		µg/dm^3	<0.02	
Benzo(a)anthracene		µg/dm^3	<0.006	
Chrysene		µg/dm^3	<0.003	
Benzo(b)fluoranthene		µg/dm^3	<0.006	
Benzo(k)fluoranthene		µg/dm^3	<0.001	
Benzo(a)pyrene		µg/dm^3	<0.001	
Dibenzo (a,h)anthracene		µg/dm^3	<0.006	
Benzo(q,h,i)perylene		µg/dm^3	<0.006	
Indeno(1,2,3-cd)pyrene		µg/dm^3	<0.02	

[1]Target value for limit of quantification is 30 % from the maximum concentration given in Decree of Ministry of Social Affairs and Health 17.11.2015/1352.

[2] The following PCBs were analysed, which sum of them were higher than the detection limit of the method: PCB-28, PCB-29, PCB-47

Soil and sediment samples

In Finland, general recommendations on analysis methods and limits of quantification have been given to ensure comparability of measurement results for soil contaminants. As a general recommendation for soil samples, the limit of quantification should not be more than 50 % of the reference value (threshold value/lower guideline value/higher guideline value given in the Government Decree on the Assessment of Soil Contamination and Remediation Needs (214/2007). However, the significance of the limit of quantification is assessed case-by-case. (Ministry of the Environment 2014)

Detection limits of the Russian standard methods were compared to recommended limits of quantification in Finland (Table 4). Russian detection limits in soil samples are lower than minimum recommendation level for limits of quantification in Finland for all contaminants except antimony listed in the Finnish Government Decree on the Assessment of Soil Contamination and Remediation Needs (214/2007).

In Finland, there are no recommendations regarding the limit of detection or quantification for sediment analyses but the Russian detection limits can be compared to the Finnish recommendations given to soil analysis. Same Russian analytical methods were used for sediment and soil samples and the detection limits are the same for soil and sediment samples.

Table 4. Comparison of detection limits of the Russian standard methods for soil and sediment to the recommended limits of the quantification for soil samples in Finland.* Detection limit of the Russian standard method is higher than recommended limit of the quantification in Finland.

Component	Method of research	Detection limits (mg/kg)	Recommended method in Finland*	Recommended limit of quantification in Finland (mg/kg)*
Vanadium (V)	М-МВИ-80-2008	<5	Pre-treatment: ISO 12914:2012 SFS-EN 16174:2012 SFS-ISO 11466:2007 Analysis: SFS-ISO 22036:2013 CEN/TS 16171:2012[3]	50
Cadmium (Cd)	М-МВИ-80-2008	<0.05		0.5
Cobalt (Co)	М-МВИ-80-2008	<0.5		10
Copper (Cu)	М-МВИ-80-2008	<0.5		50
Arsenic (As)	М-МВИ-80-2008	<0.05		1
Nickel (Ni)	М-МВИ-80-2008	<0.5		20
Lead (Pb)	М-МВИ-80-2008	<0.5		30
Antimony (Sb)	М-МВИ-80-2008	<1		0.5
Chromium (Cr)	М-МВИ-80-2008	<0.5		50
Zinc (Zn)	М-МВИ-80-2008	<0.5		100
Barium (Ba)	М-МВИ-80-2008	<5		
Manganese (Mn)	М-МВИ-80-2008	<0.5		
Molybdenum (Mo)	М-МВИ-80-2008	<1		
Strontium (Sr)	М-МВИ-80-2008	<0.5		
Water content	ГОСТ 28268-89			
LOI	ГОСТ 27784-88			
Mercury (Hg)	ПНД Ф 16.1:2.23-2000	<0.005	Pre-treatment: SFS-EN 16174:2012 SFS-ISO 11466:2007 Analysis: SFS-ISO 16772:2007	0.2
Benzo(a)pyrene	ПНД Ф 16.1:2:2.2:2.3:3.39-2003	<0.005	SFS-ISO 18287:2007	0.1
Total PAH	Information not received		SFS-ISO 18287:2007	7.5[4]
pH salt	ГОСТ 26483-85			
Oil products	ПНД Ф 16.1:2.2.22-98	<50	SFS-EN ISO 16703:2011	150
Phenols	ПНД Ф 16.1:2:3:3.44-05	<0.05	SFS-ISO 14154:2007	0.25 (monochlorophenols) 0.25 (dichlorophenols) 0.25 (trichlorophenols) 0.25 (tetrachlorophenols) 0.25 (pentachlorophenol)
Total PCB[1]	ФР.1.31.2004.01277	<0.01	SFS-ISO 10382:2007 ISO 13876:2013	0.05[1]
Total PCDD-PCDF (WHO-TEQ)	PND F 16.1:2:2.2:3.56-08	0.00000004-0.00000096[6]	ISO 13914:2013[5]	0.000005

Component	Method of research	Detection limits (mg/kg)	Recommended method in Finland*	Recommended limit of quantification in Finland (mg/kg)*
Alpha-HCH	ПНД Ф 16.1:2.2:2.3:3.61-09	<0.001		
Gamma-HCH (Lindane)	ПНД Ф 16.1:2.2:2.3:3.61-09	<0.001	SFS-ISO 10382:2007	0.005
Heachlorobenzene	ПНД Ф 16.1:2.2:2.3:3.61-09	<0.001		0.005
Heptachlor	ПНД Ф 16.1:2.2:2.3:3.61-09	<0.001		0.005
DDD	ПНД Ф 16.1:2.2:2.3:3.61-09	<0.001		0.05[2]
4,4-DDT	ПНД Ф 16.1:2.2:2.3:3.61-09	<0.001		0.05[2]
DDE	ПНД Ф 16.1:2.2:2.3:3.61-09	<0.001		0.05[2]
Grain size	ГОСТ 12536-79			

** Source: Ministry of the Environment 2014

[1] In Russia: sum of congeners 28, 52, 101, 138, 153 and 180. In Finland: sum of congeners 28, 52, 101, 118, 138, 153 and 180.
[2] Sum of dichlorodiphenyltrichloroethane (p, p'-DDT) and its metabolites (o, p'-DDT, p, p'-DDE, o, p'-DDE, o, p'-DDD and p, p'-DDD).
[3] For zinc, only SFS-ISO 22036:2013
[4] Total PAH content including the following compounds: anthracene, acenaphthene, acenaphthylene, benzo (a) anthracene, benzo (a) pyrene, benzo (b) fluoranthene, benzo (g, h, i) perylene, benzo (k) fluoranthene, dibenzo (a, h) anthracene, phenanthrene, fluoranthene, fluorene, indeno (1,2,3-c, d) pyrene, chrysene, naphthalene and pyrene.
[5] In Finland: Total concentration as WHO toxicity equivalent, including PCDD / Fs and dioxin-like PCBs (in Russia dioxin-like PCBs are not included to the analysis).
[6] Detection limits are specified for different compounds and samples in analysis reports.

4. Results of the quality control samples at the first sampling stage

Eighteen quality control samples in total were taken in the first sampling phase. Twelve of the samples ensured the quality of soil sampling and two of the samples the quality of sediment sampling. For surface water, three samples and for groundwater one sample were taken for quality assurance purposes. The number of the field duplicate samples were 14 in total. In addition, two project standards and two blank samples were included in the quality assurance process. The location of the field duplicate samples are presented in a map (Fig. 1). The soil duplicate samples were taken from both sampling depths, thus for the soil duplicates there are only five locations shown in the map.

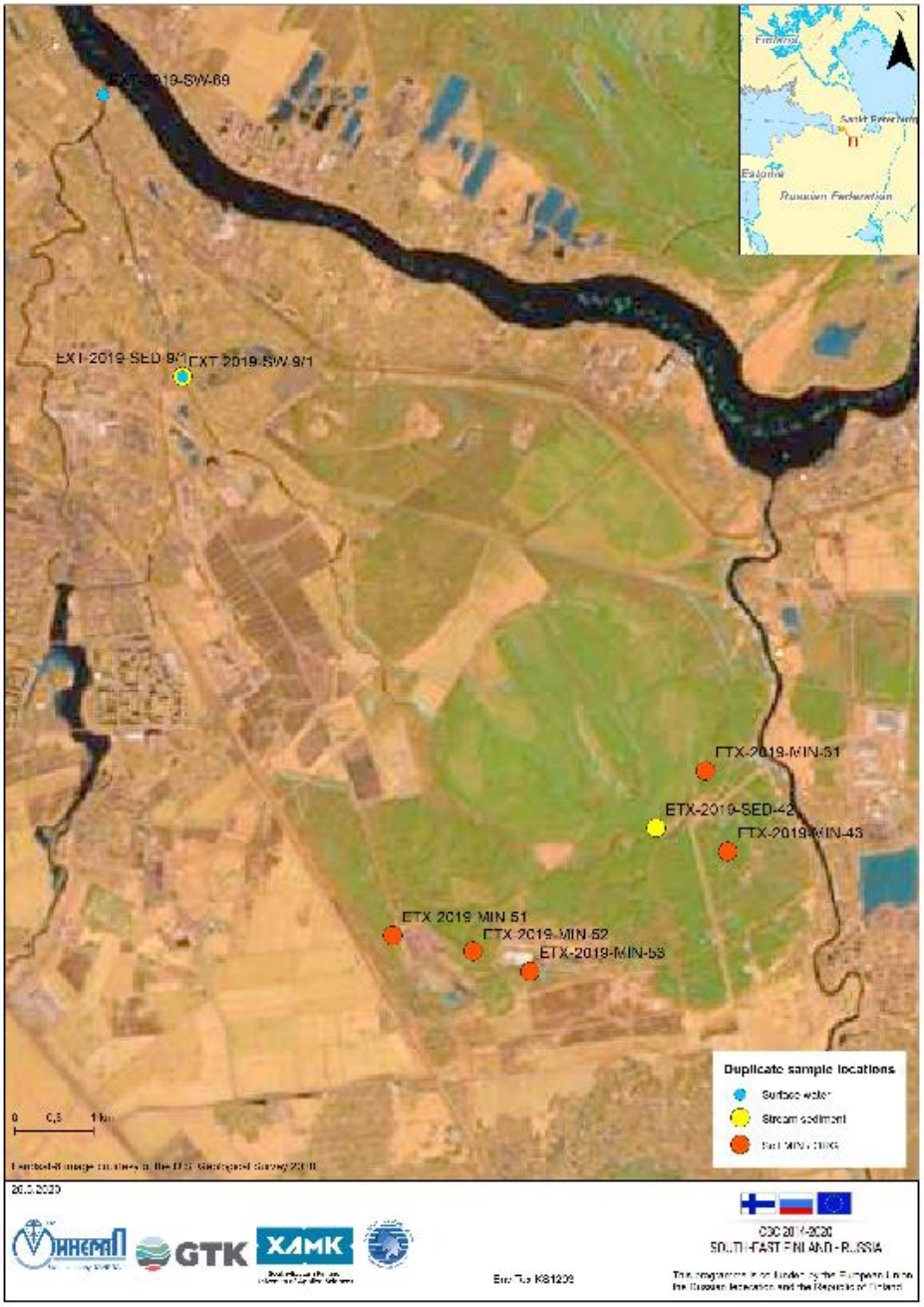

Figure 1. The location of the duplicate samples taken at the first sampling phase in the EnviTox project.

5.1 Soil

Duplicate samples

Five duplicate soil samples were taken from the both sampling depths. The minimum and maximum difference per cents between the routine and duplicate sample results are shown in the Table 5. The difference per cents were calculated only in those element values which were above the limit of

quantification. The duplicate soil samples were taken from the sampling sites 31, 43, 51, 52 and 53 (see Fig. 1).

In general, the highest differences between the element concentrations of routine and duplicate sample are in the sample pair close to the illegal landfill area (ETX-2019-ORG-52) as well as in the sample pair taken west of the illegal landfill area (ETX-2019-ORG-51). The deviations in analysis results in sample pairs taken from the depth of 0 – 5 cm are higher than in those taken from 5 – 20 cm. There is a big difference in the amounts of the organic matter in the routine sample of ETX-2019-ORG-52, LOI 10.1 % and in its field duplicate sample ETX-2019-ORG-52, LOI 90.8 %. The pH value in the routine sample ETX-2019-ORG-51, 3.75, differs remarkably from the pH value of the field duplicate sample ETX-2019-ORG-51D, 4.17.

Table 5. The minimum and maximum difference per cents between routine and duplicate soil samples taken and analysed (< 1mm grain size, 5M HNO_3 leach) in the first sampling phase of the EnviTox project. The difference per cents were calculated only in those element values which were above the limit of quantification.

	Difference between routine sample and duplicate sample			
Element or property	**Soil 0 – 5 cm**		**Soil 5 – 25 cm**	
	Minimum %	**Maximum %**	**Minimum %**	**Maximum %**
Water content	12.9	80.7	8.4	40.7
LOI	1.8	88.9	0.54	26.0
pH salt	2.6	15.2	0.90	14.1
Arsenic (As)	7.1	81.4	17.7	59.0
Barium (Ba)	-	-	-	-
Cadmium (Cd)	9.8	75.3	28.1	58.4
Cobalt (Co)	6.7	94.9	8.3	68.3
Chromium (Cr)	10.0	50.0	5.9	82.1
Copper (Cu)	5.3	79.3	21.1	67.7
Mercury (Hg)	5.6	79.2	0	59.3
Manganese (Mn)	10.2	84.8	11.7	80.9
Molybdenum (Mo)	-	-	-	-
Nickel (Ni)	5.1	82.9	0	88.0
Lead (Pb)	9.1	95.2	15.8	50.0
Antimony (Sb)	-	-	-	-
Strontium (Sr)	-	-	-	-
Vanadium (V)	-	-	-	-
Zinc (Zn)	0	86.2	11.5	42.3
Benzo(a)pyrene	-	-	-	-
Oil products	2.2	63.2	-	-
Phenols	5.3	81.3	4.8	69.5
Total PCB	-	-	-	-
Alpha-HCH	-	-	-	-
Gamma-HCH	-	-	-	-
Hexachlorobenzene	-	-	-	-
Heptachlor	-	-	-	-
DDD	-	-	-	-
4,4-DDT	-	-	-	-
DDE	-	-	-	-
Number of sample pairs	5	5	5	5

The Thompson-Howarth –plots are used to estimate the sampling variance and repeatability of sampling. The graph is produced to show the relation between the mean concentrations of routine and field duplicate sample pairs, and the absolute difference of the sample pairs. In natural soil parent material, the precision below 20 % is considered as accepted variance in sampling and repeatable. However, the homogeneity of soil samples varies and might cause higher difference between the routine and field duplicate samples. In the first sampling phase, the LOI and pH values were the only properties of performed measures and analyses whose precision was below 20 %, in general (Figures 2 and 3). The precision of metal concentrations in soil sample pairs was usually above 20 % (Figures 4 and 5) and these sample pairs could not be considered repeatable. Many metals are known to bind in organic matter. Thus, the varying amount of organic matter in the routine sample and in the field duplicate sample may explain the differences in the element concentrations.

In most cases, the concentrations of organic compounds in the field duplicate sample pairs were below the limit of quantification. The Thompson-Howarth plots were prepared only of a few compounds in which the concentrations were above the limit of quantification. All the generated Thompson-Howarth plots are presented in Appendix 1. Benzo(a)pyrene was detected only in the duplicate sample pairs taken from the 0 – 5 cm depth (Fig. 6). According to the diagram of benzo(a)pyrene, the analysis repeatability of the routine sample and duplicate sample is deficient. However, the repeatability of phenols in the duplicate soil sample pairs is rather good (Fig. 7) while the precision in most of the pairs is below 20 %.

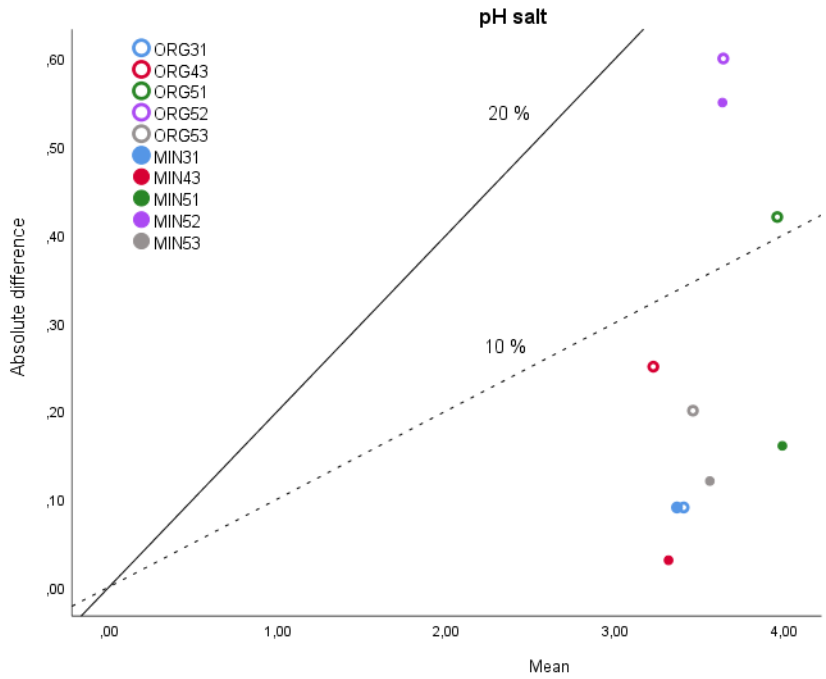

Figure 2. Thompson-Howarth -plot of pH values in soil in the 1st sampling phase of the EnviTox-project. The mean pH value of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm.

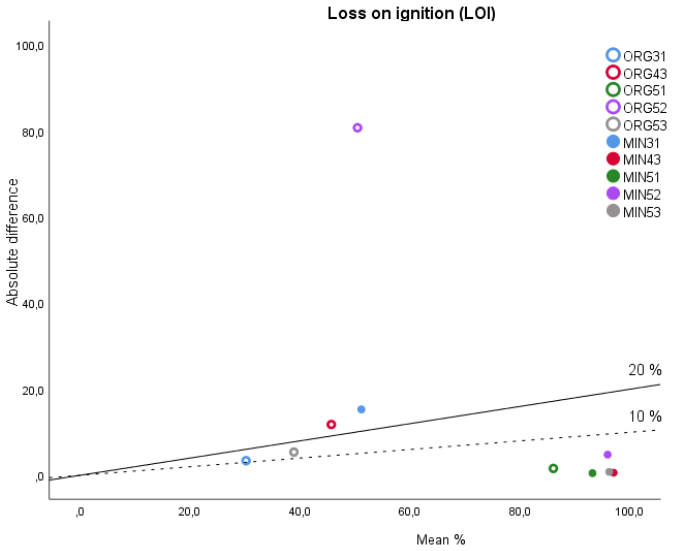

Figure. 3. Thompson-Howarth-plot of Loss on Ignition (LOI) concentrations in soil in the 1st sampling phase of the EnviTox-project. The mean LOI concentrations of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm.

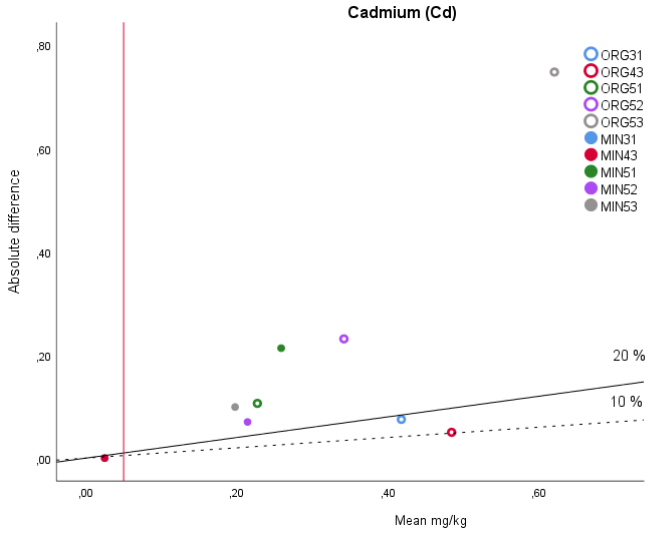

Figure 4. Thompson-Howarth-plot of Cd concentrations in soil in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean Cd concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. The red line = limit of quantification for Cd (0.05 mg/kg). In calculations, individual values with concentrations below the limit of quantification were converted to half of the limit of quantification. Thus, the sample pairs MIN31 and MIN43 appears below the limit of quantification line in the diagram.

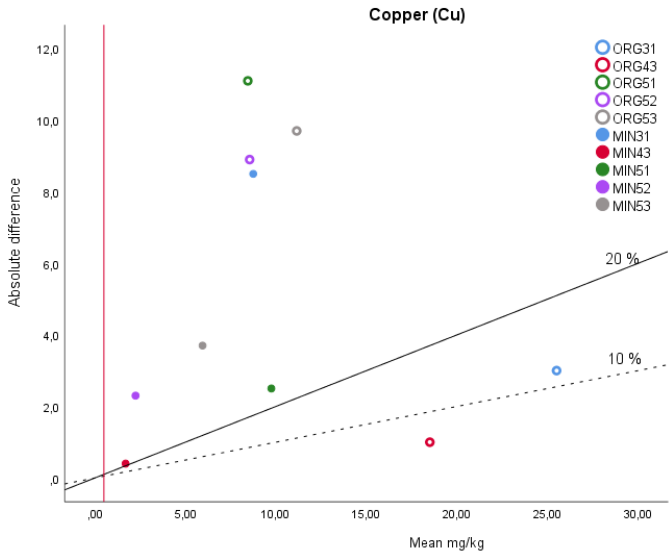

Figure 5. Thompson-Howarth-plot of Cu concentrations in soil in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean Cu concentrations of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. The red line = limit of quantification for Cu (0.5 mg/kg).

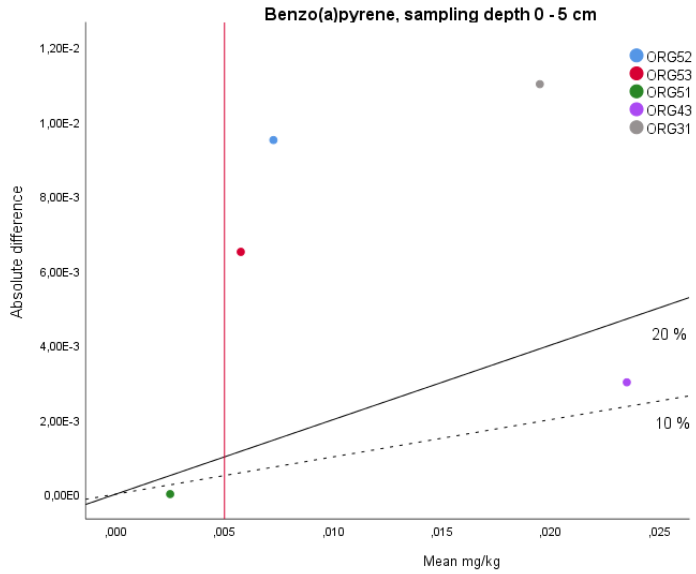

Figure 6. Thompson-Howarth-plot of benzo(a)pyrene concentrations in soil in the 1st sampling phase of the EnviTox-project. The mean benzo(a)pyrene concentrations of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm. The red line = limit of quantification for benzo(a)pyrene (0.005 mg/kg). In calculations, individual values with concentrations below the limit of quantification were converted to half of the limit of quantification. Thus, the sample pair ORG51 appears below the limit of quantification line in the diagram.

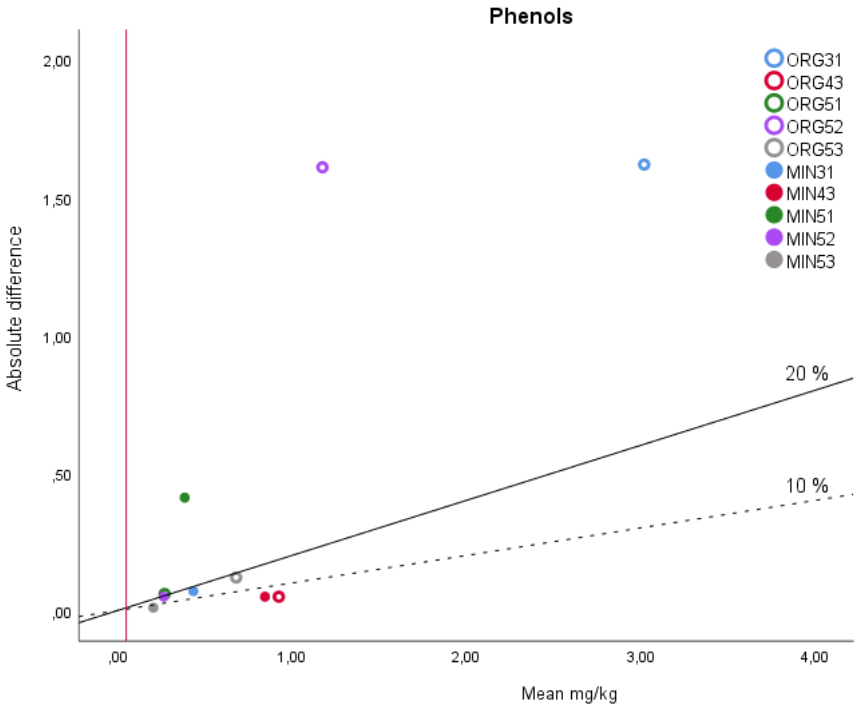

Figure 7. Thompson-Howarth-plot of phenol concentrations in soil in the 1st sampling phase of the EnviTox-project. The mean phenol concentrations of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. The red line = limit of quantification for phenols (0.05 mg/kg).

Project standard sample

Two project standards were added to the sample set when all the soil samples had been taken. The project standard was a soil reference sample prepared by GTK. It is dried and homogenized soil material from the Pirkanmaa region in Finland. While the analysis method for metals used in the 1st sampling phase of the EnviTox project differ from the Finnish analysis methods, the analysis results of the project standard could not be compared to the GTK's previous analysis results of the standard sample.

While the sample pre-treatment and analysis methods for metals used in Russia differ from the ones in Finland, there were not any comparable metal analysis results for the reference sample results available from previous studies. That is why three samples of the project standard material was sieved in grain size below 1 mm and sent to the Finnish laboratory for 5M HNO_3 and 14M HNO_3 extractions. The element concentrations in these three reference samples were also analysed using *aqua regia* extraction method from the fraction size below 2 mm as well as the fraction size below 1 mm. All the project standards used in the EnviTox project as well as their analysis methods are assembled in Table 6.

The metal and some other element concentrations of the project standard sample analysed from different grain sizes and with different analysis methods are presented in Table 7. The comparison of the results show that the concentration of the acid used in the extraction is not a satisfactory explanation to such high variation in the metal concentrations.

Table 6. The project standards and the analysis methods used in the 1st sampling phase in the EnviTox project.

Reference sample	Fraction	Leaching method	Analysis period	Laboratory
Project standard 1	Grain size < 2 mm	*Aqua regia* extraction	October 2019	Finnish
	Grain size < 1 mm	*Aqua regia* extraction	November 2019	Finnish
	Grain size < 1 mm	5M HNO_3 extraction	May-June 2020	Finnish
	Grain size < 1 mm	14M HNO_3 extraction	May-June 2020	Finnish
Project standard 2	Grain size < 2mm	*Aqua regia* extraction	October 2019	Finnish
	Grain size < 1 mm	*Aqua regia* extraction	November 2019	Finnish
	Grain size < 1 mm	5M HNO_3 extraction	May-June 2020	Finnish
	Grain size < 1 mm	14M HNO_3 extraction	May-June 2020	Finnish
Project standard 3	Grain size < 2mm	*Aqua regia* extraction	October 2019	Finnish
	Grain size < 1 mm	*Aqua regia* extraction	November 2019	Finnish
	Grain size < 1 mm	5M HNO_3 extraction	May-June 2020	Finnish
	Grain size < 1 mm	14M HNO_3 extraction	May-June 2020	Finnish
Project standard Russia 1	Grain size < 1 mm	5M HNO_3 extraction	Autumn 2019	Russian
Project standard Russia 2	Grain size < 1 mm	5M HNO_3 extraction	Autumn 2019	Russian

Table 7. The element concentrations of the EnviTox project standard samples analysed from different grain sizes and with different analysis methods in Russian and Finnish laboratories.

	Project standard 1 (ETX-2019-MIN-100)	Project standard 2 (ETX-2019-MIN-100/1)	Project standard 1 – 3			
Laboratory	Russian	Russian	Finnish	Finnish	Finnish	Finnish
Grain size	< 1 mm	< 1 mm	< 1 mm	< 1 mm	< 1 mm	< 2mm
Extraction	5M HNO_3	5M HNO_3	5M HNO_3	14M HNO_3	*Aqua regia*	*Aqua regia*
Analysis method			Leach in microwave owen, ICP-MS and ICP-OES technique	Leach in microwave owen, ICP-MS and ICP-OES technique	AR-leach 90 °C, ICP-MS and ICP-OES technique	AR-leach 90 °C , ICP-MS and ICP-OES technique
			Min - Max	Min - Max	Min - Max	Min - Max
Unit	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Antimony (Sb)	< 1	< 1	0.05 – 0.06	<0.02	0.14 – 0.19	0.14 – 0.41
Arsenic (As)	9.1	3.3	26.0 – 27.9	25.9 – 27.8	25.1 – 25.8	23.2 – 25.6
Barium (Ba)	< 5	< 5	39.1 – 42.8	33.9 – 40.9	30.5 – 33.3	32.4 – 39.6
Cadmium (Cd)	< 0.05	< 0.05	0.08 – 0.10	0.08 – 0.11	0.07	0.07 – 0.08
Cobalt (Co)	3.2	3.9	5.2 – 5.5	5.1 – 6.2	4.8 – 5.0	4.8 – 5.9
Copper (Cu)	17	18	20.4 – 21.5	20.6 – 22.3	21.5 – 24.9	19.8 – 22.6
Chromium (Cr)	13	14	24.5 – 26.4	26.3 – 27.6	22.4 – 23.6	23.6 – 24.8
Lead (Pb)	2.1	3.9	4.8 – 5.4	4.9 – 5.7	4.5 – 4.6	3.9 – 4.7
Manganese (Mn)	67	72	165 – 189	169 – 186	155 – 158	162 – 165
Molybdenum (Mo)	< 1	< 1	15.4 – 15.6	14.7 – 16.4	1.5 – 1.6	1.4 – 1.7

	Project standard 1 (ETX-2019-MIN-100)	Project standard 2 (ETX-2019-MIN-100/1)	Project standard 1 – 3			
Nickel (Ni)	7.4	8.6	11.3 – 12.0	11.5 – 13.4	11.8 – 12.5	12.1 – 13.3
Strontium (Sr)	< 0.5	< 0.5	11.7 – 17.9	12.4 – 20.3	5.8 – 6.5	6.2 – 6.7
Vanadium (V)	< 5	< 5	35.3 – 38.5	34.8 – 38.5	32.3 – 33.0	32.6 – 36.5
Zinc (Zn)	26	28	25.3 – 28.9	25.8 – 31.7	34.0 – 35.0	34.0 – 39.0
Number of samples	1	1	3	3	3	3

5.2 Stream sediments

Duplicate samples

Two field duplicate samples were taken for the quality assurance purposes of the stream sediment sampling. The difference per cents between routine and duplicate sample results are shown in the Table 8. The difference per cents were calculated only in those element values which were above the limit of quantification.

The differences between the stream sediment sample pairs were more moderate than those in soils. The highest variation is in the concentrations of cadmium and phenols. In general, the difference per cents in metal concentrations were higher in the sample pair taken from the downstream in the north of the study area (ETX-2019-SED-9/1) and the difference per cents in oil products, phenols, DDD and total PAH concentrations were higher in the southern sample pair (Table 8).

Table 8. The difference per cents between the normal and the duplicate stream sediment samples taken and analysed (< 1mm grain size, 5M HNO_3 leach) in the first sampling phase of the EnviTox project. The difference per cents were calculated only in those element values which were above the limit of quantification.

	Difference between routine sample and duplicate sample	
Element or property	**Stream sediment**	
	Duplicate sample 1 (ETX-2019-SED-9/1) %	**Duplicate sample 2 (ETX-2019-SED-42) %**
Water content	41.5	32.2
LOI	6.2	14.8
pH salt	4.1	0.20
Arsenic (As)	46.4	16.3
Barium (Ba)	-	-
Cadmium (Cd)	74.5	71.9
Cobalt (Co)	56.0	23.5
Chromium (Cr)	26.2	18.7
Copper (Cu)	53.6	40.0
Mercury (Hg)	9.5	41.8
Manganese (Mn)	48.0	16.5
Molybdenum (Mo)	-	-
Nickel (Ni)	46.4	15.0
Lead (Pb)	37.5	46.2

	Difference between routine sample and duplicate sample	
Element or property	**Stream sediment**	
	Duplicate sample 1 (ETX-2019-SED-9/1) %	**Duplicate sample 2 (ETX-2019-SED-42) %**
Antimony (Sb)	-	-
Strontium (Sr)	-	-
Vanadium (V)	26.2	51.4
Zinc (Zn)	45.8	37.4
Benzo(a)pyrene	15.7	13.8
Oil products	1.9	36.4
Phenols	56.7	62.8
Total PCB	-	-
Alpha-HCH	-	-
Gamma-HCH	-	-
Hexachlorobenzene	-	-
Heptachlor	-	-
DDD	-	16.7
4,4-DDT	-	-
DDE	-	-
Total PAH	29.7	58.2

The Thompson-Howarth –plots were generated for the routine and field duplicate sample pairs of sediments. Similar to soil parent material, the precision below 20 % is considered as accepted variance and repeatability of sampling in the natural environmental conditions. However, the heterogeneity in the environment, naturally or anthropogenic based, may cause higher differences between the routine and field duplicate samples. In the first sampling phase, the LOI and pH values were the only properties of performed measures and analyses whose precision was below 20 %. The precision of metal concentrations in sediment sample pairs was usually above 20 % and these sample pairs could not be considered repeatable. However, the precision of mercury and oil products in a sample pair of 9/1 and the precision of manganese, arsenic and nickel in all sample pairs were below 20 %, and thus sampling variance can be considered small and repeatability is good. All the generated Thompson-Howarth plots are presented in Appendix 1.

5.3 Surface water

Duplicate samples

Two field duplicate samples were included in the surface water sample batches for the quality assurance purposes. The difference per cents between routine and duplicate sample results are shown in the Table 8. The difference per cents were calculated only in those element values which were above the limit of quantification.

The highest variation between the results of the sample pair 9/1 is in ammonium, lead, cobalt and total PCB concentrations. In the sample pair 69, the highest difference per cents were in aluminium, lead, BOD, iron and vanadium, concentrations (Table 9).

Table 9. The difference per cents between the normal and the duplicate surface water samples taken and analysed in the first sampling phase of the EnviTox project. The difference per cents were calculated only in those element values or properties which were above the limit of quantification.

	Difference between routine sample and duplicate sample	
Element or property	**Stream water**	
	Duplicate sample 1 (ETX-2019-SW-9/1) %	**Duplicate sample 2 (ETX-2019-SW-69) %**
pH	0.0	0.0
Temperature	0.0	0.0
Electric Conductivity	0.0	0.0
Dissolved Oxygen	0.0	0.0
COD	21.9	23.8
BOD 5 days	33.3	33.3
BOD total	35.7	33.3
Ammonium NH_4	56.8	17.5
Nitrites NO_2	-	-
Nitrates NO_3	15.4	16.7
Sulphates SO_4^{2-}	14.2	6.4
Chloride Cl^-	0.0	0.0
Fluoride F^-	0.0	0.0
Hydrocarbonate HCO_3^-	0.0	2.6
Cyanide	-	-
Evaporated residue	3.9	3.8
Suspended substances	37.5	25.0
Hydrogensulphide H_2S	-	-
Sulphides S_2	-	-
Formaldehyde	-	-
Surface active anionic substances	-	-
Phenols	-	-
Oil products total	-	-
Mercury Hg	-	-
Chrome Cr^{3+}	-	-
Chrome Cr^{6+}	-	-
Cadmium Cd	-	-
Nickel Ni	-	-
Lead Pb	58.9	48.7
Common Iron Fe	14.3	34.6
Manganese Mn	8.6	20.8
Copper Cu	11.1	27.3
Zinc Zn	-	-
Cobalt Co	≥58.3	≥15,4
Aluminium Al	15.1	68.4
Vanadium V	30.8	30.6
Calcium Ca	9.5	3.0
Magnesium Mg	11.8	10.8
Potassium K	7.1	7.7
Sodium Na	12.2	5.9
Benzo(a)pyrene	-	-
DDT sum of isomers	-	-

	Difference between routine sample and duplicate sample	
Element or property	**Stream water**	
	Duplicate sample 1 (ETX-2019-SW-9/1) %	**Duplicate sample 2 (ETX-2019-SW-69) %**
Total PCB	45.1	22.8
Trichloroethylene	-	-
Chloroform	-	-
Bromide Br	-	-
Total PAH	-	-
Organic carbon	4.8	0.0
Napthalene	-	-
Acenaphthene	-	-
Fluorene	-	-
Phenanthrene	-	-
Anthracene	-	-
Fluoranthene	-	-
Pyrene	-	-
Benzo(a)anthracene	-	-
Chrysene	-	-
Benzo(b)fluoranthene	-	-
Benzo(k)fluoranthene	-	-
Benzo(a)pyrene	-	-
Dibenzo(a,h)anthracene	-	-
Benzo(q,h,i)perylene	-	-
Indeno(1,2,3-cd)pyrene	-	-

The Thompson-Howarth –plots were generated for the routine and the field duplicate sample pairs. Similar to minerogenic sampling materials, the precision below 20 % is considered as accepted variance and repeatability of sampling in the natural environmental conditions. However, the heterogeneity in the environment, naturally or anthropogenic based, may cause higher differences between the routine and field duplicate samples. In the first sampling phase, the precision of evaporated residues, organic carbon as well as all the main anion and cation concentrations are below the 20 % and thus sampling variance can be considered small and repeatability good. The precision of BOD values, suspended substances and surface active anionic substances are above 20 % in the studied sample pairs. The Fe and Mn precision of the sample pair ETX-2019-SW-9/1 is below the 20 % but the precision of the sample pair ETX-2019-SW-69 above the 20 %. In general, the precision of metal concentrations is above 20 %. All the generated Thompson-Howarth plots are presented in Appendix 1.

Blank sample

A field blank sample controls cumulatively the quality of sampling, the influence of the environment, the possibility of cross-contamination of samples at the sampling site, during transportation and storage as well as the quality of sampling equipment, distilled water and the acid used for preservation of the samples.

For the surface water sampling quality assurance, one blank sample was taken. The parameter selection of the blank sample analysis contained altogether 43 element or compound concentrations as well as water properties. In general, the element concentrations in a blank sample is expected to be below the limits of quantification, but in our blank sample the lead concentration 47 µg/l and Hg 1.0 µg/l were measured. Thus,

the lead and mercury concentrations in the surface water samples of the 1st sampling phase should be considered only suggestive. Minor concentrations of manganese, copper, aluminium, magnesium as well as total PCB and organic carbon were also measured in this blank sample. In comparison to the Russian quality standards for distilled water (Table 10), the ammonium concentration in the blank sample (0.14 mg/l) is above the standard value (< 0.02 mg/l). The limit of quantification for the evaporated residue in water samples in Envitox project were 50 mg/l. Thus, the concentration of evaporated residue in the blank sample, < 50 mg/l is not comparable with the distilled water standard value, <5 mg/l.

Table 10. The quality standards for distilled water (GOST 6709-96) in Russia.

Element or property	Standard value
Mass concentration of the residue after evaporation, mg/l	<5
Mass concentration of ammonium (NH_4) and ammonium salts, mg/l	<0.02
Mass concentration of nitrate (NO_3), mg/l	<0.2
Mass concentration of sulphate (SO_4), mg/l	<0.5
Mass concentration of chloride (Cl), mg/l	<0.02
Mass concentration of aluminium (Al), mg/l	<0.05
Mass concentration of iron (Fe), mg/l	<0.05
Mass concentration of calcium (Ca), mg/l	<0.8
Mass concentration of copper (Cu), mg/l	<0.02
Mass concentration of lead (Pb), mg/l	<0.05
Mass concentration of zinc (Zn), mg/l	<0.2
Mass concentration of substances reducing $KMnO_4$, mg/l	0.08
pH	5.4 – 6.6
Electric conductivity at 20 °C S/m	$<5 * 10^{-4}$

Ion balance

The ratio of anion and cation sums, ion balances of the surface water samples were calculated as a part of the quality assurance process. However, usually surface waters are so unstable that the ion balances are not a reliable way to prove the quality of the sampling and analysis process. Thus, these results are not presented here.

5.4 Groundwater

Duplicate sample

For groundwater sampling quality assurance, no duplicate samples were taken.

Blank sample

One blank sample was taken for the quality assurance of groundwater sampling. Only 14 metal concentrations were analysed of this blank sample. From this blank sample 14 µg/l nickel was detected and minor amounts of sodium and potassium.

Ion balance

The ratio of anion and cation sums, ion balances of the groundwater samples were calculated. The formula used in calculations:

Anion sum = HCO_3 meq/l + Cl meq/l + SO_4 meq/l + NO_3 meq/l

Cation sum = Ca meq/l + Mg meq/l + K meq/l + Na meq/l)

Ion balance = the ratio of the anion sum and the cation sum

All the ion balance per cents of the five groundwater samples were below 5 %, which shows that the quality of the groundwater analyses is good and reliable.

The ratio of evaporated dry residues and sum of seven main ions was calculated as well:

Evaporated dry residue value ≈ HCO_3 mg/l + Cl mg/l + SO_4 mg/l + NO_3 mg/l + Ca mg/l + Mg mg/l + K mg/l + Na mg/l

According to the ratio of the evaporated dry residue and the sum of seven main ions, the balance showed good convergence (Table 11).

Table 11. The ratio of the experimental dry residue and the sum of seven main ions (HCO_3 mg/l + Cl mg/l + SO_4 mg/l + NO_3 mg/l + Ca mg/l + Mg mg/l + K mg/l + Na mg/l).

Groundwater sample	Evaporated residue mg/l	The sum of 7 main ions mg/l	Ratio
ETX-2019-GW-81	379	473	1.25
ETX-2019-GW-82	617	746	1.21
ETX-2019-GW-83	469	544	1.16
ETX-2019-GW-84	360	453	1.26
ETX-2019-GW-85	244	338	1.38

6. Results of the quality control in the laboratory

6.1. Quality control standards

All the samples were analysed by the accredited laboratory PTK-Analytic LLC in St. Petersburg. The certification for accreditation (given in July 2015) is available in the laboratory´s web page (ptk-analitik.com) and proves that the laboratory meets the requirements of the standards GOST ISO / IEC 17025-2009. In 2017 and 2019, the laboratory passed the qualification confirmation procedure and expanded the scope of the accreditation.

PTK-Analytic LCC commissioned PAH analyses from the Typhoon LLC, Environmental Monitoring Center “ARLEX”, which is under the authority of ROSHYDROMET (Federal Hydrometeorological and Environmental Monitoring Unit), NPO (Scientific Production Association). The laboratory has an accreditation certificate and the details are given in the analysis reports.

PTK-Analytic LCC commissioned bromide-ion and organic carbon analyses of water samples from the Federal State Budgetary Institution (FSBI), Laboratory Center of Analysis and Technical Measurements in the North-

Western Federal District. The laboratory has an accreditation certificate and the details are given in the analysis reports.

The analysis of dioxins and furans in 5 samples was carried out in Chemistry-Analytical Centre "Arbitration", D.I. Mendeleev Institute, St. Petersburg. Laboratory has the accreditation.

The personnel of the EnviTox project was responsible for the sampling, storing and transporting the samples. The laboratory was not responsible for following these steps. Laboratory refers to standard sampling procedures in the analysis reports.

Analyses were performed according to the Russian standards listed in Table 12. The laboratory use the approved methodology only within the scope of its distribution, which is prescribed in the text of the methodology. E.g. the methodology can only apply to groundwater or only to surface water. Same analytical methods were used for soil and sediment samples. Detailed information about used measuring devices are given in the analysis reports.

The laboratory confirms that the measurement conditions are in accordance with the requirements of the ND methodology. (ND = normative documents)

Table 12. Standard methods used in the analysis of elements/compounds from different sample matrices.

Analysis	Soil	Sediment	Stream water	Groundwater
Barium (Ba)	M-MVI-80-2008	M-MVI-80-2008		
Vanadium (V)			PND F 14.1: 2: 4.214-06	RD 52.24.377-2008
Cadmium (Cd)			PND F 14.1: 2: 4.214-06	M-03-505-119-08
Cobalt (Co)			PND F 14.1: 2: 4.214-06	M-03-505-119-08
Manganese (Mn)			PND F 14.1: 2: 4.214-06	M-03-505-119-08
Copper (Cu)			PND F 14.1: 2: 4.214-06	M-03-505-119-08
Molybdenum (Mo)				
Arsenic (As)				
Nickel (Ni)			PND F 14.1: 2: 4.214-06	M-03-505-119-08
Lead (Pb)			PND F 14.1: 2: 4.214-06	M-03-505-119-08
Strontium (Sr)				
Antimony (Sb)				
Chromium (Cr)			PND F 14.1: 2: 4.52-96[1]	PND F 14.1: 2: 4.52-96[1]
Zinc (Zn)			PND F 14.1: 2: 4.214-06	M-03-505-119-08
Water content	GOST 28268-89	GOST 28268-89		
LOI	GOST 27784-88	GOST 27784-88		
Mercury (Hg)	PND F 16.1: 2.23-2000	PND F 16.1: 2.	PNDF 14.1: 2: 4.160-2000	PNDF 14.1: 2: 4.160-2000
Benzo(a)pyrene	PND F 16.1: 2: 2.2: 2.3: 3.39-2003	PND F 16.1: 2: 2.2: 2.3: 3.	PND F 14.1: 2: 4.186-02	PND F 14.1: 2: 4.186-02
pH salt	GOST 26483-85	GOST 26483-85		
Oil products	PND F 16.1: 2.2.22-98	PND F 16.1: 2.2.22-98	PND F 14.1: 2: 4.5-95	FR 1.31.2011.11315
Phenols	PND F 16.1: 2: 3: 3.44-05	PND F 16.1: 2: 3: 3.44-05	PND F 14.1: 2: 4.182-2002	PND F 14.1: 2: 4.182-2002
Total PCB	FR.1.31.2004.01277	FR.1.31.2004.01277	PND F 14.1: 2: 3: 4.204-04	PND F 14.1: 2: 3: 4.204-04
PCDD/PCDF	PND F 16.1:2:2.2:3.56-08	PND F 16.1:2:2.2:3.56-08		
Alpha-HCH	PND F 16.1: 2.2: 2.3: 3.61-09	PND F 16.1: 2.2: 2.3: 3.61-09		
Gamma-HCH				
Hexachlorobenzene				
Heptachlor				

Analysis	Soil	Sediment	Stream water	Groundwater
DDD				
4,4-DDT			PND F 14.1: 2: 3: 4.204-04 (DDT sum of isomers)	PND F 14.1: 2: 3: 4.204-04 (DDT sum of isomers)
DDE				
Grain size	GOST 12536-79	GOST 12536-79		
Total PAH	The results are not received	FR. 1.31.2004.01279	PND F 14.1: 2: 4.70-96[2]	PND F 14.1: 2: 4.70-96[2]
COD			PND F 14.1: 2: 4.190-2003	
BOD 5 days			PND F 14.1: 2.275-2012	
BOD total				
Ammonium (NH_4^+)			RD 52.24.383-2018	RD 52.24.383-2018
Nitrites (NO_2^-)			RD 52.24.381-2017	RD 52.24.381-2017
Nitrates (NO_3^-)			RD 52.24.380-2017	RD 52.24.380-2017
Sulphate (SO_4^{2-})			RD 52.24.405-2005	PND F 14.1: 2.159-2000
Chloride ions (Cl^-)			PND F 14.1: 2: 4.111-97	RD 52.24.407-2017
Fluoride ion (F^-)			PND F 14.1: 2: 4.270-2012	PND F 14.1: 2: 4.270-2012
Hydrocarbonate (HCO_3^-)			PND F 14.1: 2: 3.99-97	PND F 14.1: 2: 3.99-97
Cyanide ion			PND F 14.1: 2.56-96	
Evaporated residue			PND F 14.1: 2: 4.114-97	PND F 14.1: 2: 4.114-97
Suspended substances			PND F 14.1: 2: 4.254-2009	
Hydrogen sulphide (H_2S)			RD 52.24.450-2010	РД 52.24.450-2010
Sulphides (S^{2-})				RD 52.24.368-2006
Formaldehyde			PND F 14.1: 2.4.84-96	
Surface active anionic substances			PND F 14.1: 2: 4.15-95	RD 52.24.368-2006
Common iron			PND F 14.1: 2: 4.214-06	M-03-505-119-08
Aluminium (Al)			PND F 14.1: 2: 4.214-06	M-03-505-119-08
Calcium (Ca)			PND F 14.1: 2: 4.137-98	PND F 14.1: 2: 4.137-98
Magnesium (Mg)				
Potassium (K)			PND F 14.1: 2: 4.138-98	PND F 14.1: 2: 4.138-98
Sodium (Na)				
Trichloroethylene			RD 52.24.482-2012	RD 52.24.482-2012
Chloroform				
Bromides (Br-)			PND F 14.2: 4.176-2000	PND F 14.2: 4.176-2000
Organic carbon			GOST 31958-2012	
Odor				RD 52.24.496-2018
Colour				PND F 14.1: 2: 4.207-04
Turbidity				PND F 14.1: 2: 3: 4.213-05
Total hardness				RD 52.24.395-2017
Permanganate oxidation				PND F 14.1: 2: 4.154-99
Alkalinity				GOST 31957-2012

[1] Chrome (Cr^{3+}) and Chrome (Cr^{6+}) were analysed separately.

[2] Including: Naphthalene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Dibenzo(a,h)anthracene, Benzo(q,h,i)perylene, Indeno(1,2,3-cd)pyrene. Concentrations are analysed for each compound in addition to total PAH concentration.

6.2. Uncertainty of measurements

The measurement uncertainty indicates the maximum possible single analytical result deviation from the reference value and it is usually reported as 95 % confidence level. The measurement uncertainty consists of the combined effect of a random error and of a systematic error. Random error can be an effect of minor differences in the reagent additions, variation in the cleanliness of laboratory equipment and the environment, the instability of measuring instruments reading accuracy, temperature fluctuations, and different calibration solutions. Systematic error can be an effect of sample instability between sampling and analysis, inability to determine all essential forms of an analyte, disturbances e.g. sample matrix, incorrect calibration, and invalid blank correction. Typically, the measurement uncertainty is proportional to the concentration. (Kahelin 2015)

Laboratory (PTK-Analytic LCC) has reported measuring uncertainty (error) in the analysis reports and the error is specific for each sample. Error is given as a concentration (± from measured concentration). The given error corresponds to the accuracy indicator with a reliable probability of 0.95. According to given values, the uncertainty of measurements was calculated as percentages for each of analysed elements/compounds and samples and compared to Finnish recommendations.

Laboratory (Typhoon LLC) has not reported measuring uncertainty for total PAH analysis. Chemistry-Analytical Centre "Arbitration", D. I. Mendeleev Institute has not reported laboratory- or analysis specific measuring uncertainty for PCDD/PCDF analysis. However, according to the method (PND F 16.1:2:2.2:3.56-08) the measurement error is 80 % for the range of 1-10 ng/kg and 60 % for the range of 10-1000 ng/kg.

Stream water samples

According to the requirements of the Finnish Government Decree on Substances Dangerous and Harmful to the Aquatic Environment 23.11.2006/1022. Annex 3, the level of measurement uncertainty shall not exceed 50 %.

The measurement uncertainty (as percentages) calculated from the error values reported by the laboratory were typically under 50 %. There was variation in measurement uncertainty between samples but values exceeding 50 % were reported only for few samples (Table 13).

Table 13. The uncertainty of measurements (range and median %) of analysed elements/compounds in stream water samples, which exceed the detection limit.

Component	Uncertainty of measurements Minimum - Maximum	Median	Number of samples
COD	14-32 %	20 %	22
BOD 5 days	26-40 %	26 %	21
BOD total	19-33 %	26 %	21
Ammonium (NH_4^+)	3-21 %	5 %	23
Nitrites (NO_2^-)	15-33 %	16 %	14
Nitrates (NO_3^-)	9-70 %	25 %	21
Sulphates (SO_4^{2-})	12-17 %	12 %	22
Chloride ions (Cl^-)	9-13 %	10 %	23
Fluoride ion (F^-)	9-20 %	17 %	20
Hydrocarbonate (HCO_3^-)	8-21 %	11 %	24

Component	Uncertainty of measurements Minimum - Maximum	Median	Number of samples
Cyanide ion	44-45 %	45 %	2
Evaporated residue	5-19 %	9 %	24
Suspended substances	9-21 %	13 %	24
Hydrogen sulphide (H_2S)	All values under the detection limit		
Sulphides (S^{2-})	All values under the detection limit		
Formaldehyde	22 %	22 %	1
Surface active anionic substances	18-38 %	21 %	18
Phenols	33-52 %	50 %	18
Oil products. total	All values under the detection limit		
Mercury (Hg)	19-53 %	30 %	23
Chrome (Cr^{3+})	38-42 %	40 %	6
Chrome (Cr^{6+})	All values under the detection limit		
Cadmium (Cd)	All values under the detection limit		
Nickel (Ni)	19-32 %	21 %	15
Lead (Pb)	19-43 %	24 %	14
Common Iron (Fe)	17-23 %	20 %	24
Manganese (Mn)	18-41 %	20 %	25
Copper (Cu)	27-43 %	40 %	23
Zinc (Zn)	19-43 %	31 %	16
Cobalt (Co)	27-33 %	31 %	3
Aluminium (Al)	27-33 %	30 %	25
Vanadium (V)	20-52 %	37 %	15
Calcium (Ca)	10-24 %	15 %	24
Magnesium (Mg)	12-25 %	14 %	25
Potassium (K)	8-23 %	19 %	17
Sodium (Na)	10-18 %	15 %	24
Benzo(a)pyrene	All values under the detection limit		
DDT (sum of isomers)	All values under the detection limit		
Total PCB	34-51 %	35 %	25
Trichloroethylene	9 %	9 %	1
Chloroform	7-12 %	11 %	12
Bromides (Br^-)	10-27 %	25 %	8
Total PAH including:	Error values are not given		
Naphthalene	Error values are not given		
Acenaphthene	Error values are not given		
Fluorene	Error values are not given		
Phenanthrene	Error values are not given		
Anthracene	Error values are not given		
Fluoranthene	Error values are not given		
Pyrene	Error values are not given		
Benzo(a)anthracene	Error values are not given		
Chrysene	Error values are not given		

Component	Uncertainty of measurements Minimum - Maximum	Median	Number of samples
Benzo(b)fluoranthene	Error values are not given		
Benzo(k)fluoranthene	Error values are not given		
Benzo(a)pyrene	Error values are not given		
Dibenzo(a,h)anthracene	Error values are not given		
Benzo(q,h,i)perylene	Error values are not given		
Indeno(1,2,3-cd)pyrene	Error values are not given		
Organic carbon	14-21 %	19 %	25

Groundwater samples

In Finland, the permissible measurement uncertainties of drinking water analyses have been defined in the Decree of Ministry of Social Affairs and Health 17.11.2015/1352 and is not allowed to exceed values shown in Table 3. Uncertainty of measurement reported by the laboratory was higher than maximum allowable values in the Finnish guidelines for sulphates, mercury, aluminium and sodium in some of the samples (Table 14).

Table 14. The uncertainty of measurements (median, range %) for analysed elements/compounds in groundwater samples, which exceed the detection limit. *Uncertainty of measurement reported by laboratory is higher than maximum allowable values according to Decree of Ministry of Social Affairs and Health 17.11.2015/1352.

Analysed element/compound	Uncertainty of measurements			Maximum allowable uncertainty of measurements (%) FIN[4]
	Range	Median	Number of samples	
Odor		Error values are not given		
Colour	18-33 %	29 %	5	
Turbidity	20 %	20 %	3	30 %
Total hardness	6-7 %	6 %	5	
Permanganate oxidation	9-21 %	11 %	5	50 % (COD_{Mn})
Alkalinity	11-12 %	12 %	5	
Ammonium (NH_4^+)	11 %	11 %	1	
Nitrites (NO_2^-)		All values under the detection limit		
Nitrates (NO_3^-)	15-30 %	10 %	5	
Sulphates (SO_4^{2-})	**14-20 %***	**15 %**	**5**	**15 %**
Chloride ions (Cl^-)	7-11 %	9 %	4	15 %
Fluoride ion (F^-)	10-18 %	18 %	4	20 %
Hydrocarbonate (HCO_3^-)	11 %	11 %	5	
Evaporated residue	9 %	9 %	5	
Hydrogen sulphide (H_2S)		All values under the detection limit		
Sulphides (S^{2-})		All values under the detection limit		
Surface active anionic substances	27-70 %	64 %	3	

Analysed element/compound	**Uncertainty of measurements**			**Maximum allowable uncertainty of measurements (%) FIN[4]**
Phenols	50 %	50 %	3	
Oil products. total		All values under the detection limit		
Mercury (Hg)	**31-53 %***	**50 %**	**3**	**30 %**
Chrome (Cr^{3+})		All values under the detection limit		30 % (chrome)
Chrome (Cr^{6+})		All values under the detection limit		
Cadmium (Cd)		All values under the detection limit		25 %
Nickel (Ni)	10-16 %	15 %	4	25 %
Lead (Pb)		All values under the detection limit		25 %
Common Iron (Fe)	20-23 %	22 %	4	30 %
Manganese (Mn)	12-16 %	13 %	4	30 %
Copper (Cu)	25 %	25 %	1	25 %
Zinc (Zn)	17-21 %	20 %	5	
Cobalt (Co)		All values under the detection limit		
Aluminium (Al)	**19-32 %***	**31 %**	**5**	**25 %**
Vanadium (V)	32-43 %	37 %	5	
Calcium (Ca)	15-16 %	15 %	5	
Magnesium (Mg)	13-15 %	13 %	5	
Potassium (K)	17-22 %	20 %	5	
Sodium (Na)	**14-18 %***	**17 %**	**5**	**15 %**
Benzo(a)pyrene	40 %	40 %	1	50 %
DDT (sum of isomers)		All values under the detection limit		30 % (pesticides)[2]
Total PCB	49-52 %	50 %	5	
Trichloroethylene		All values under the detection limit		40 %
Bromides (Br^-)	24-28 %	27 %	3	
Total PAH including:		All values under the detection limit		50 %[3]
Naphthalene		All values under the detection limit		
Acenaphthene		All values under the detection limit		
Fluorene		All values under the detection limit		
Phenanthrene		Error values are not given		
Anthracene		All values under the detection limit		
Fluoranthene		All values under the detection limit		
Pyrene		All values under the detection limit		
Benzo(a)anthracene		All values under the detection limit		
Chrysene		All values under the detection limit		
Benzo(b)fluoranthene		All values under the detection limit		
Benzo(k)fluoranthene		All values under the detection limit		
Benzo(a)pyrene		All values under the detection limit		
Dibenzo(a,h)anthracene		All values under the detection limit		
Benzo(q,h,i)perylene		All values under the detection limit		
Indeno(1,2,3-cd)pyrene		All values under the detection limit		

[1] If the value of the measurement uncertainty cannot be reached, the best available technique (maximum 60 %) must be chosen.
[2] Performance values for individual pesticides are indicative. Low values for measurement uncertainty (up to 30%) can be achieved for several pesticides. Higher values (up to 80 %) may be allowed for certain pesticides.
[3] The performance values refer to individual substances defined as 25 % of the maximum value of the variable.
[4]Finnish Government Decree on Substances Dangerous and Harmful to the Aquatic Environment 23.11.2006/1022. Annex 3.

Soil samples

There are no recommendations for uncertainty of measurements concerning soil analyses in Finland. Uncertainty of measurement reported by the laboratory was around 30 % for metals (except mercury). Highest measurement uncertainties (median values) were reported for pesticides (around 50 %). However, for many substances, there was considerable variation in the measurement uncertainty between samples. (Table 15). For dioxins and furans, the measurement error according to the method (PND F 16.1:2:2.2:3.56-08) is 80 % for the range of 1-10 ng/kg and 60 % for the range of 10-1000 ng/kg.

Table 15. The uncertainty of measurements (range and median %) for analysed elements/compounds in organic (0-5 cm) and mineral soil (5-20 cm) samples, which exceed the detection limit.

Analysed element/compound	**Uncertainty of measurements Soil 0-5 cm**			**Uncertainty of measurements Soil 5-20 cm**		
	Range	**Median**	**Samples**	**Range**	**Median**	**Samples**
Barium (Ba)	All values under the detection limit			All values under the detection limit		
Vanadium (V)	29-31 %	30 %	10	29-31 %	30 %	8
Cadmium (Cd)	3-31 %	30 %	68	29-31 %	30 %	45
Cobalt (Co)	3-33 %	30 %	59	25-333 %	30 %	50
Manganese (Mn)	27-305 %	30 %	66	27-31 %	30 %	68
Copper (Cu)	28-33 %	30 %	66	25-33 %	30 %	68
Molybdenum (Mo)	29-31 %	29 %	3	29-30 %	30 %	2
Arsenic (As)	0-36 %	31 %	70	26-40 %	30 %	71
Nickel (Ni)	27-33 %	30 %	66	29-33 %	30 %	65
Lead (Pb)	27-33 %	30 %	66	27-33 %	30 %	68
Strontium (Sr)	All values under the detection limit			All values under the detection limit		
Antimony (Sb)	All values under the detection limit			All values under the detection limit		
Chromium (Cr)	27-43 %	30 %	76	28-40 %	30 %	76
Zinc (Zn)	27-33 %	30 %	76	27-33 %	30 %	78
Water content	Error values are not given			Error value given only for 4 samples		
LOI	Error values are not given			Error values are not given		
Mercury (Hg)	0-46 %	25 %	76	3-50 %	45 %	76
Benzo(a)pyrene	3-44 %	31 %	48	11-41 %	28 %	15
pH salt	1-3 %	3 %	76	0-3 %	3 %	76
Oil products	24-26 %	25 %	33	25-26 %	25 %	10
Phenols	18-28 %	20 %	66	18-50 %	20 %	66
Total PCB	29-50 %	35 %	13	All values under the detection limit		
Alpha-HCH	All values under the detection limit			Error value is not given		
Gamma-HCH	45 %	45 %	2	All values under the detection limit		

Analysed element/compound	Uncertainty of measurements Soil 0-5 cm			Uncertainty of measurements Soil 5-20 cm		
	Range	**Median**	**Samples**	**Range**	**Median**	**Samples**
Hexachlorobenzene	4-100 %	50 %	19	33-50 %	50 %	3
Heptachlor	33-50 %	48 %	7	20-50 %	50 %	10
DDD	46-57 %	49 %	4	40-50 %	50 %	4
4,4-DDT	43-50 %	50 %	13	50 %	50 %	6
DDE	33-50 %	50 %	13	50 %	50 %	7
Grain size	Not determined			Error values are not given		

Sediment samples

For metals, the measurement uncertainty was about 30 %. For organic compounds (and mercury), reported measurement uncertainties were higher but typically less than 50 % (except for heptachlor, DDD and 4,4-DDT max. 60-67 %) (Table 16). For dioxins and furans, the measurement error according to the method (PND F 16.1:2:2.2:3.56-08) is 80 % for the range of 1-10 ng/kg and 60 % for the range of 10-1000 ng/kg. In Finland, no specific recommendations are given regarding measurement uncertainty of sediment analysis.

Table 16. Uncertainty of measurements (%) of analysed elements/compounds in sediment samples. which exceed the detection limit.

Analysed element/compound	Uncertainty of measurements		
	Range	Median	Number of samples
Ba	all values under detection limit		
V	29-31 %		
Cd	29-33 %	30 %	22
Co	28-33 %		
Mn	30 %	30 %	24
Cu	28-31 %	30 %	24
Mo	29-33 %	31 %	8
As	25-40 %	33 %	24
Ni	27-33 %	30 %	24
Pb	28-31 %	30 %	24
Sr	all values under detection limit		
Sb	all values under detection limit		
Cr	29-33 %	30 %	24
Zn	30 %	30 %	24
Hg	20-50 %	44 %	24
Benzo(a)pyrene	28-44 %	38 %	20
Oil products	25 %	25 %	18
Phenols	20-45 %	20 %	24
Total PCB	40-50 %	43 %	7
Alpha-HCH	33-50 %	50 %	5
Gamma-HCH	33-44 %	43 %	3
Hexachlorobenzene	50 %	50 %	5
Heptachlor	40-67 %	40 %	5
DDD	33-60 %	40 %	15
4,4-DDT	33-67 %	40 %	17
DDE	33-50 %	40 %	13

Analysed element/compound	Uncertainty of measurements		
	Range	Median	Number of samples
Total PAH	Error values are not given		
Water content	Error values are not given		
LOI	Error values are not given		
Grain size	Error values are not given		
pH salt	1 – 2 %	2 %	24

6.3. Replicate measurements

According to the Field Manual, laboratory is responsible for their own quality control (including replicate samples when sample is analysed twice) and reporting for the project personnel. Laboratory standard samples (based on laboratory guidelines, 5 % at minimum) are part of the quality control of the study as well. However, there is no specific mention about replicate samples/analysis performed by the laboratory in the analysis reports.

Replicate analyses were ordered from laboratory for few soil samples. Duplicate samples were taken from five sampling points (point 31, 43, 51, 52 and 53) from both organic (0 – 5 cm) and mineral (5 – 20 cm) layers. All these samples (total 20 samples) were analysed (pH, As, Cd, Cr, Hg, Zn and benzo(a)pyrene) as two replicates (total 40 replicate measurements). Results were analysed with Thompson-Howarth-plots and statistically by Anova (see Chapter 6). According to Thompson-Howarth-plots (Appendix 1), the repeatability of pH analysis is very good while the precision of all the replicates is below 20 % (Fig. 8). For the analysed metals, the analytical repeatability is good as well (Figures 9 and 10). Only the precision of Cd in samples ETX-2019-ORG-43D and ETX-2019-ORG-53 is above 20 %. In samples ETX-2019-ORG-43D, ETX-2019-MIN-31, ETX-2019-MIN-31D, ETX-2019-MIN-52 and ETX-2019-MIN-53, the precision of Hg is above 20 % (Fig. 10). The Thompson-Howarth-plot of zinc in soil replicates show that for some metals, the repeatability is more deficient in concentrations close to the limit of quantification than in higher concentrations (Fig. 11).

From stream water and sediment, duplicate samples were taken from two sampling points (stream water points 9/1 and 69, sediment points 9 and 42) but replicate analyses were not carried out. From groundwater, no duplicate samples or replicate analyses were taken.

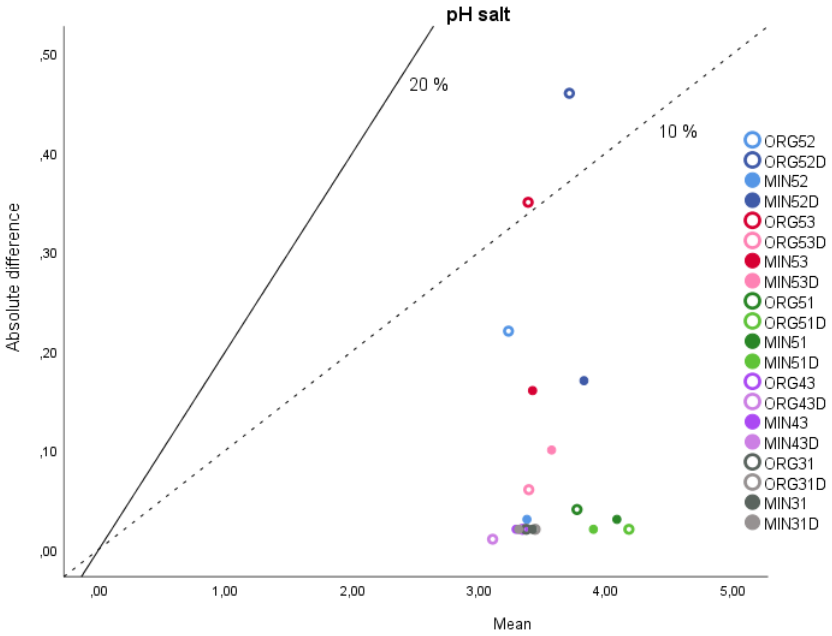

Figure 8. Thompson-Howarth-plot of pH values in soil replicate samples in the 1st sampling phase of the EnviTox-project. The mean pH value of the routine and the repeated measurement in each sample pair is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. Sample with 'D' in the sample code is the field duplicate sample of the sample with the same number.

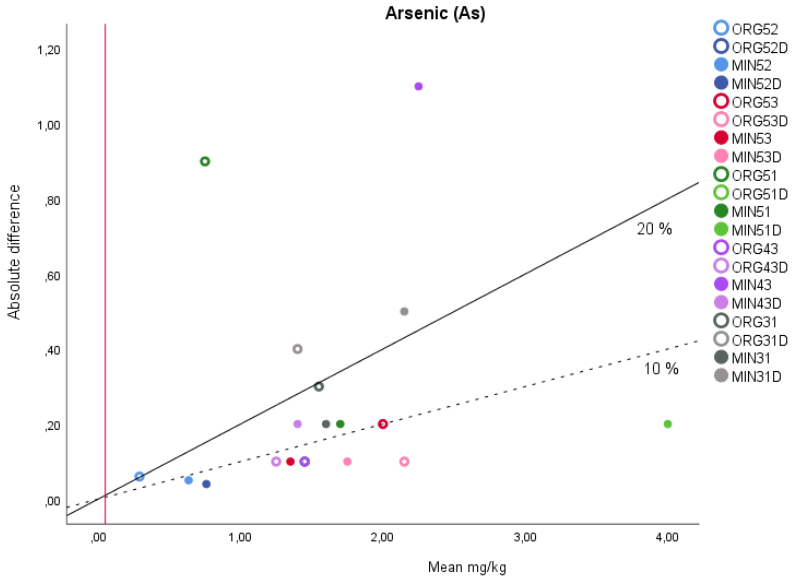

Figure 9. Thompson-Howarth-plot of As concentrations in soil replicate samples in the 1st sampling phase of the EnviTox-project (< 1 mm, grain size, 5 M HNO_3 extraction). The mean As concentration of the routine and repeated analysis is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. Sample with 'D' in the sample code is the field duplicate sample of the sample with the same number. The red line = limit of quantification for As (0.05 mg/kg).

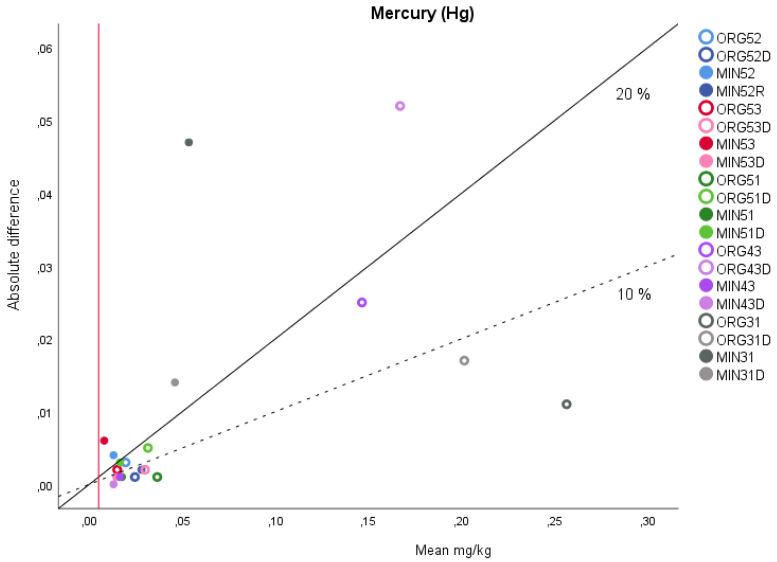

Figure 10. Thompson-Howarth-plot of Hg concentrations in soil replicate samples in the 1st sampling phase of the EnviTox-project (< 1 mm, grain size, 5 M HNO_3 extraction). The mean Hg concentrations of the routine and repeated analysis is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. Sample with 'D' in the sample code is the field duplicate sample of the sample with the same number. The red line = limit of quantification for Hg (0.005 mg/kg).

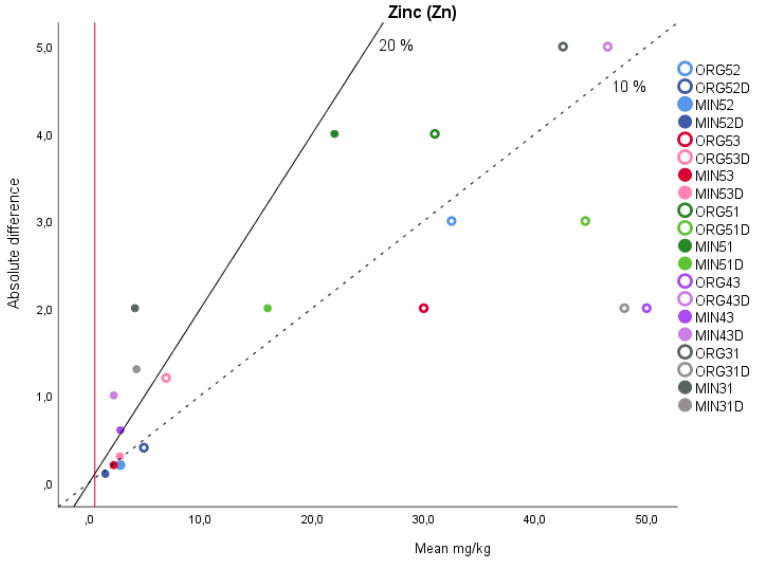

Figure 11. Thompson-Howarth-plot of Zn concentrations in soil replicate samples in the 1st sampling phase of the EnviTox-project (< 1 mm, grain size, 5 M HNO_3 extraction). The mean Zn concentrations of the routine and repeated analysis is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. Sample with 'D' in the sample code is the field duplicate sample of the sample with the same number. The red line = limit of quantification for Zn (0.5 mg/kg).

6.4. Different analytical batches

Stream water samples were taken and analysed in eight different batches. Samples were taken in August 5th – 26th, 2019. All the groundwater samples were taken and analysed in one batch. Groundwater samples were taken in October 2nd, 2019. PTK-Analytic received samples and started the analysis within one day after the sampling. Analysis lasted 20-50 days. Typhoon LLC received samples 1 – 2 days later than PTK-Analytic to make PAH-analysis and CLATI for bromide and organic carbon analysis. PAH-analysis lasted 13 – 15 days and bromide and organic carbon analysis 1 – 6 days.

Soil samples (organic layer 0 – 5 cm, mineral layer 5 – 10 cm) were taken in 12 different batches in August 5th – 26th, 2019. Organic and mineral soil samples were analysed and reported separately (total 24 batches). PTK-Analytic received the samples and started the analysis in the same day or 1 – 5 days after the sampling. Analysis lasted quite long time, about 3.5 – 5.5 months. Laboratory reports from the PAH-analysis by Typhoon LLC are not available for soil samples.

Sediment samples were taken and analysed in eight different batches. Samples were taken in August 5th – 26th, 2019 (at the same time as stream water samples). PTK-Analytic received samples and started the analysis one day after the sampling. Analysis lasted 3.5 – 4.2 months. Typhoon LLC received all the samples to total PAH analysis on in January 29th, 2020. Analysis lasted 12 days.

Dioxin/furan (PCDD/PCDF) analyses were performed for 5 selected samples in June 2020. Samples for analyses were selected according to other analytical results (especially concentrations of PCB and PAH) by project personnel.

7. Analysis of variance (ANOVA)

Analysis of variance (ANOVA) is a statistical method that can be employed to detect the mean variability among factors. ANOVA is a statistical test used to analyse the difference between the means of more than two groups. It has been suggested that sampling, analytical and geochemical variances are also presented by diagrams or in the table in order to have a clear view about the quality and reliability of geochemical data. The accepted uncertainty of sampling is usually less than 16 % and for laboratory analysis less than 4 % (e.g. Demetriades 2011).

Application of ANOVA technique to environmental surveys is particularly appropriate due to the high degree of heterogeneity often associated with anthropogenic contamination. ANOVA allows the estimation of the random errors produced by both the sampling and the analysis (Ramsey et al. 1992). A balanced ANOVA design for studying field and analytical variability require that each sample collected at a field duplicate site would be split and analysed twice (Reimann et al. 2008). This was done in the EnviTox project. The field duplicate was also taken as a separate sample, i.e. not by splitting one field sample in two parts.

In order to estimate the sampling uncertainty and to assess the precision of the chemical analysis, duplicate samples and repeat analytical measurements were taken. In the first sampling phase, approximately 10 % of all sites and sampling matrices were sampled in duplicate. Two duplicate samples were taken from sediments (22 sediment samples in total), five duplicates from soils with both sampling depths (61 soil samples in total) and two duplicate samples from surface water (23 surface water samples in total). The laboratory analysis

was repeated for each duplicate sample-pair. This ended up with four separate analysis of one sampling point.

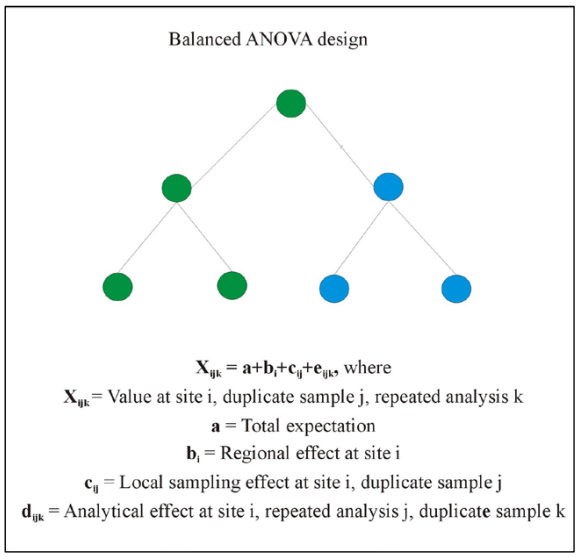

Figure 12. Quality control of sampling and analyses by replicates using ANOVA (Sandström et al. 2005)

Based on the ANOVA, the components of variance were detected between sites, between sampling depths, between duplicates and within samples. Statistical variation in element or organic compounds concentrations among various sites and sampling depths (ORG and MIN) were compared. The estimates are based on differences between mean values (Tables 17-19). The calculations were made separately for both sampling layers and for the whole data set.

When analysing the sampling layer 0 – 5 cm, the difference between sites was slightly significant for As, significant for Zn and benzo(a)pyrene and highly significant for Cr and Hg. The difference between duplicate or replicate samples was not significant for any of the substances included in the ANOVA testing (Table 17).

When analysing the sampling layer 5 – 20 cm, the difference between sites was slightly significant for As and Cr, significant for Hg and highly significant for Cd and Zn. The difference between duplicate or replicate samples was not significant for any of the substances included in the ANOVA testing (Table 18). All the concentrations of benzo(a)pyrene are below the limit of quantification.

When analysing both sampling layers, the difference between sites was slightly significant for As, Cr and benzo(a)pyrene and highly significant for Hg. The differences between two sampling layers was slightly significant for Cd, significant for Hg and highly significant for Cr, Zn and benzo(a)pyrene. The difference between duplicate or replicate samples was not significant for any of the substances included in the ANOVA testing (Table 19).

Table 17. The difference between means of sampling layer 0 – 5 cm using ANOVA.

Element/ substances	Between Sites	Between Duplicates	Between Replicates
Cd	0.133	0.663	0.099
As	0.009*	0.652	0.187
Cr	0.000***	0.951	0.833
Zn	0.001**	0.759	0.338
Hg	0.000***	0.902	0.925
Benzo(a)pyrene	0.001**	0.965	0.331

* Significance level is <0.05 and difference is slightly significant
** Significance level is <0.01 and difference is significant
*** Significance level is <0.001 and difference is highly significant

Table 18. The difference between means of sampling layer 5 – 20 cm using ANOVA.

Elements / substances	Between Sites	Between Duplicates	Between Replicates
Cd	0.000***	0.788	0.160
As	0.010*	0.965	0.240
Cr	0.027*	0.981	0.127
Zn	0.000***	0.898	0.650
Hg	0.001**	0.712	0.809
Benzo(a)pyrene	-	-	-

* Significance level is <0.05 and difference is slightly significant
** Significance level is <0.01 and difference is significant
*** Significance level is <0.001 and difference is highly significant

Table 19. The difference between means of sampling layers 0 – 5 cm and 5 – 20 cm using ANOVA.

Element / substances	Between Sites	Between Layers	Between Duplicates	Between Replicates
Cd	0.494	0.000*	0.683	0.550
As	0.018*	0.123	0.848	0.093
Cr	0.018*	0.000***	0.961	0.784
Zn	0.125	0.000***	0.876	0.476
Hg	0.000***	0.001**	0.962	0.966
Benzo(a)pyrene	0.045*	0.000***	0.970	0.408

* Significance level is <0.05 and difference is slightly significant
** Significance level is <0.01 and difference is significant
*** Significance level is <0.001 and difference is highly significant

The difference between the element concentration means of the sampling sites shows the geochemical heterogeneity of the case study area, i.e. the difference between the sites. The detected concentrations and their variety between the sites is due to geological variance and anthropogenic input. The difference between the element concentration means of two sampling layers is explained with variation in the physical characteristics of different sampling depths (organic matter content, amount of fine-grained sediment, water content) as well as with geology and anthropogenic input. Anthropogenic input is often stronger in the topmost samples and geology affect the detected element concentrations for the samples taken deeper. The difference between the element concentration means of field duplicate samples shows the geochemical

heterogeneity of the sampled sites. However, this difference is usually much less than what is seen between the sampling sites. It gives an indication of "within-site" variability (e.g. Johnson 2011). The difference between the element concentrations means of replicate samples shows the laboratory measurement uncertainty. Replicate pair is used to identify laboratory error (e.g. Johnson 2011). The difference between the element concentrations of the laboratory replicates should be very low if conducted analyses are repeatable.

In addition, the differences in pH values and in metal concentration levels between sites and inside two sampling layers (0 – 5 cm and 5 – 20 cm) were illustrated with boxplot diagrams. The difference in the pH values is clearly seen between sites (Fig. 13). A great variation in the pH values of duplicate and replicate samples can be detected in some sites (51 and 52). The cadmium concentrations do not vary significantly between sites and the variation between duplicate and replicate samples is low despite the 0 – 5 cm samples of the site 53 (Fig. 14). The arsenic concentrations are higher in the 5 – 20 cm samples showing also greater variation in measured concentrations than in the 0 – 5 cm samples (Fig. 15). The chromium concentrations in the 0 – 5 cm samples of sites 31, 43 and 51 differ from other sites and sampling layers (Fig. 16). However, the variation of concentration inside the sampling layers is not significant. The zinc concentrations in the 0 – 5 cm samples have greater variation compared with the 5 – 20 cm samples (Fig. 17). The difference in the concentrations levels between sites can also be detected. The mercury concentrations differ between sites and often between sampling layers as well (Fig. 18). The concentrations of benzo(a)pyrene are often below or very close to the limit of quantification. Thus, the conclusions of differences in concentration levels can't be made.

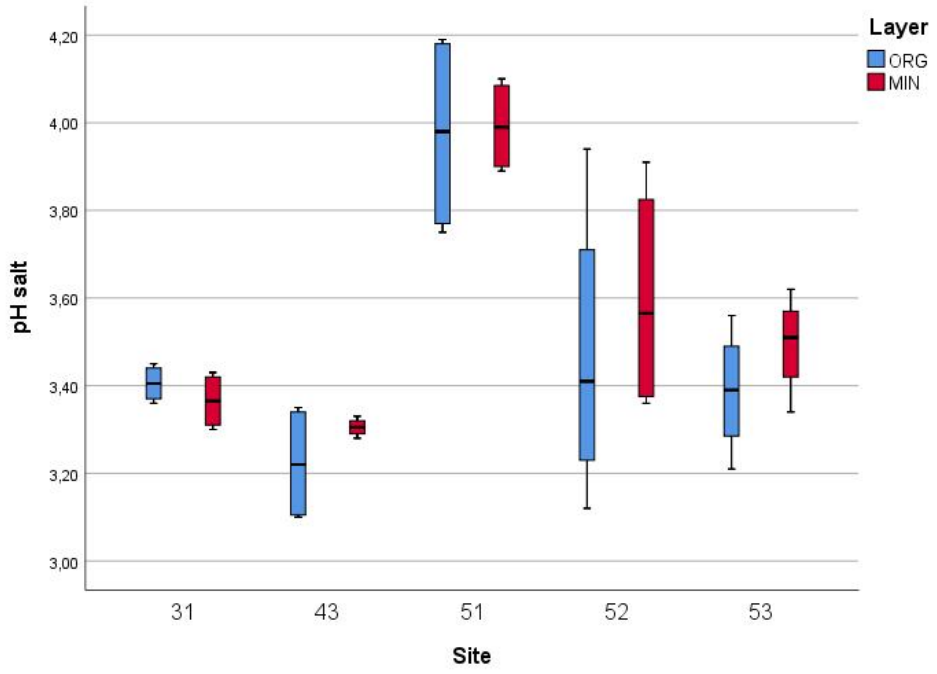

Figure 13. The distribution of pH values in soil duplicate and replicate samples in the 1st sampling phase of the EnviTox-project. The number of samples in each pillar is four (routine sample and its replicate and field duplicate sample and its replicate). ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm.

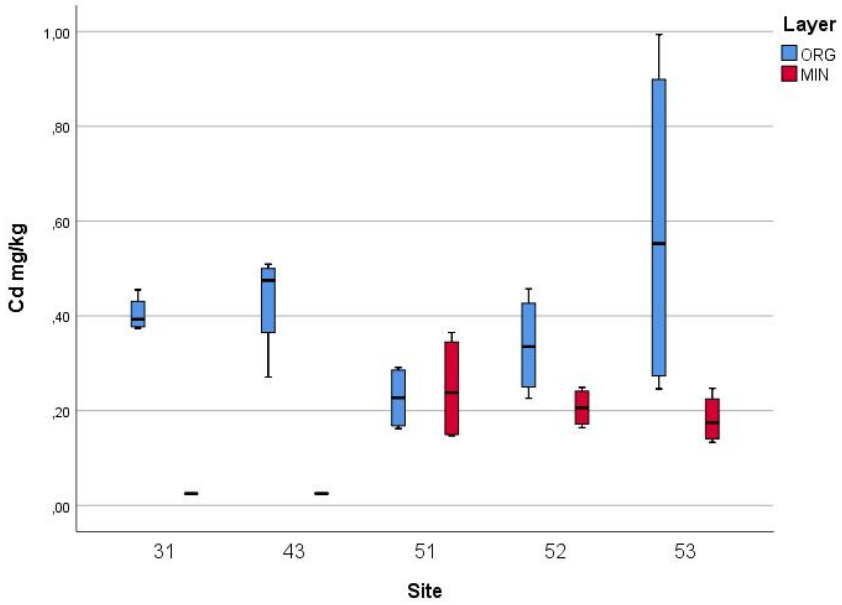

Figure 14. The distribution of Cd concentrations in soil duplicate and replicate samples in the 1st sampling phase of the EnviTox-project (< 1 mm, grain size, 5 M HNO_3 extraction). The number of samples in each pillar is four (routine sample and its replicate and field duplicate sample and its replicate). The limit of quantification for Cd is 0.05 mg/kg. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm.

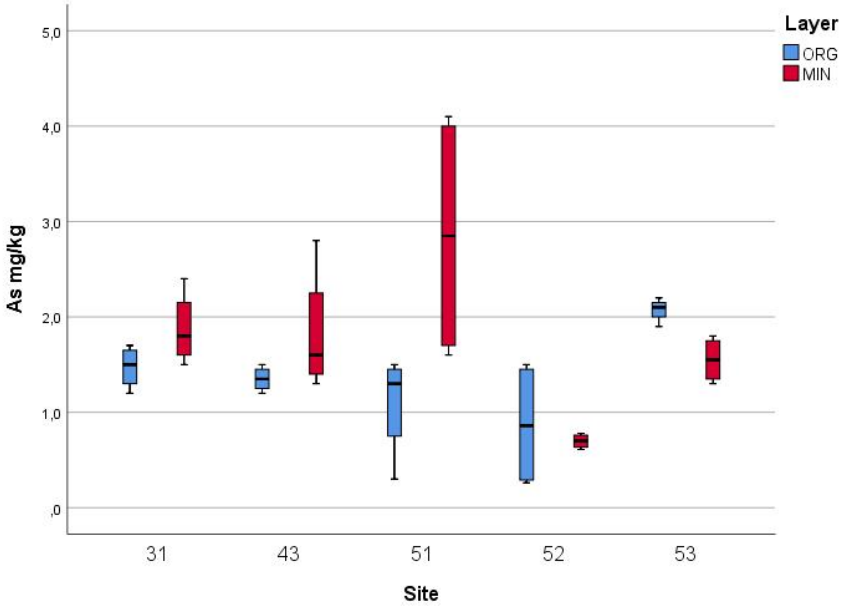

Figure 15. The distribution of as concentrations in soil duplicate and replicate samples in the 1st sampling phase of the EnviTox-project (< 1 mm, grain size, 5 M HNO_3 extraction). The number of samples in each pillar is four (routine sample and its replicate and field duplicate samples and its replicate). The limit of quantification for As is 0.05 mg/kg. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm.

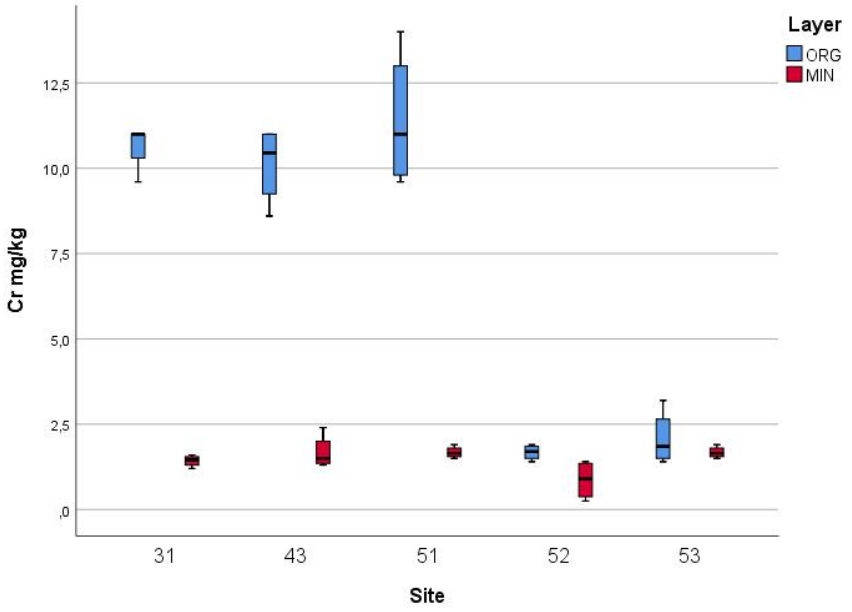

Figure 16. The distribution of Cr concentrations in soil duplicate and replicate samples in the 1st sampling phase of the EnviTox-project (< 1 mm, grain size, 5 M HNO_3 extraction). The number of samples in each pillar is four (routine sample and its replicate and field duplicate sample and its replicate).. The limit of quantification for Cr is 0.5 mg/kg. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm.

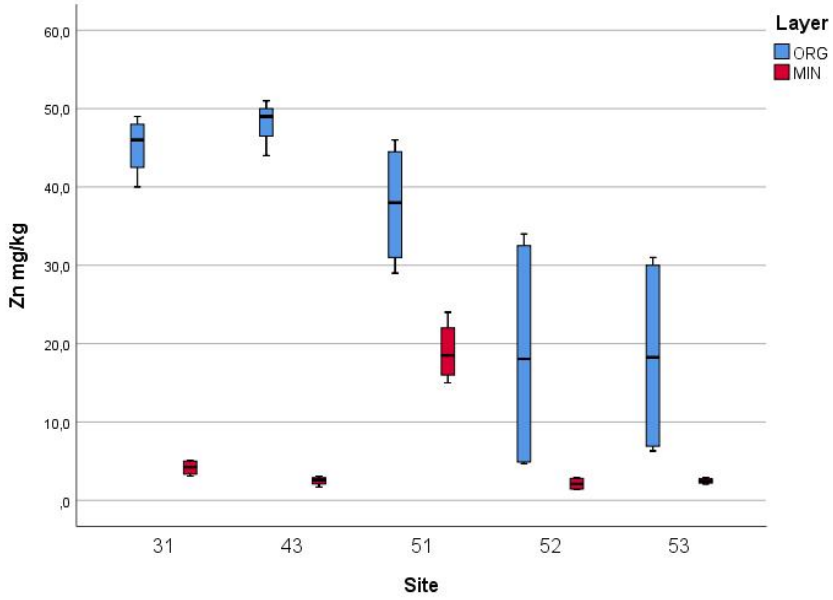

Figure 17. The distribution of Zn concentrations in soil duplicate and replicate samples in the 1st sampling phase of the EnviTox-project (< 1 mm, grain size, 5 M HNO_3 extraction). The number of samples in each pillar is four (routine sample and its replicate and field duplicate sample and its replicate). The limit of quantification for Zn is 0.5 mg/kg. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm.

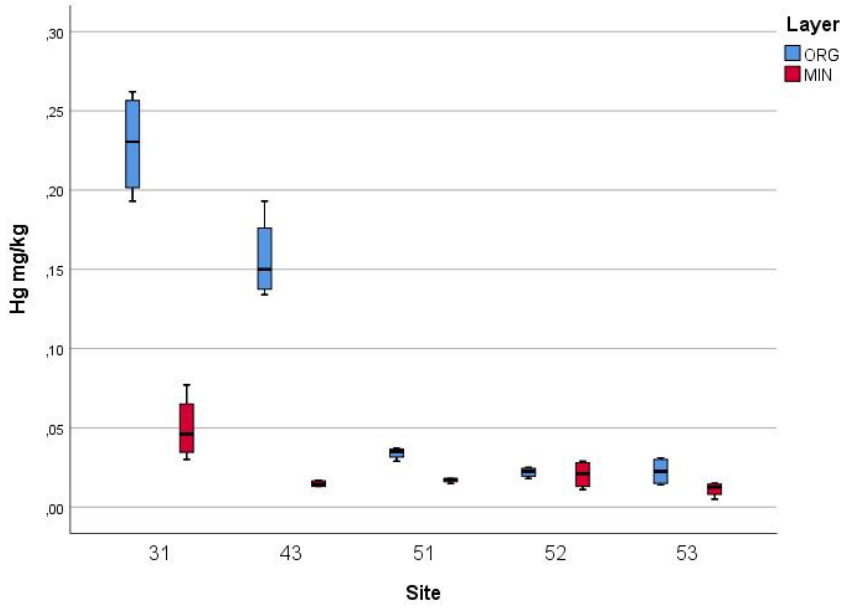

Figure 18. The distribution of Hg concentrations in soil duplicate and replicate samples in the 1st sampling phase of the EnviTox-project (< 1 mm, grain size, 5 M HNO_3 extraction). The number of samples in each pillar is four (routine sample and its replicate and field duplicate sample and its replicate). The limit of quantification for Hg is 0.005 mg/kg. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm.

8. Summary

The EnviTox project has carried out the first fieldwork and sampling phase to get information for the studies of the environmental status and potential impacts of the toxic waste landfill as well as illegal landfills and waste storage within the surroundings of Krasny Bor. Altogether 122 soil samples, 22 stream sediment samples, 22 surface water samples as well as 5 groundwater samples were taken from the project study area and analysed for several elements and compounds. The fieldwork and sampling took place in August, 2019. In addition, seven surface water and groundwater samples were taken as monitoring samples in October, 2019.

The quality assurance of the 1st sampling stage consisted of the sampling staff training and the preparation of the Sampling Guidelines as well as the field manual and the sampling plan. The quality control samples were agreed on and they included duplicate, replicate and blank samples as well as a project standard provided by GTK. In addition, in the beginning of the 1st sampling phase, all the project partners were attending to the sampling. The Finnish partners followed the sampling process and compared the sampling practices used to the Finnish standards and practices. Some challenging and complicated points in the sampling were detected and they were discussed and solved in co-operation. The laboratories that were used for analysis have the accreditation, and the analytical methods used were accredited or they were based on the Russian standards. Accredited testing laboratories enforce their own customary quality assurance methods.

The training of the sampling staff was arranged by approved trainers of Xamk in June, 2019. The training consisted of the basic theory for sampling, quality assurance and safety issues as well as practical training for

soil and water sampling and for field measurements. The guidance for sampling was gathered in the EnviTox – Guidelines for Sampling, Analysis and Quality Assurance -report (Hatakka et al. 2019). The detailed instructions for the fieldwork, for the sampling of surface water, groundwater, stream sediment and soil as well as snow and the sampling equipment, the sampling plan and the field manual were given in the appendices. The whole sampling team including attendees from GTK and Xamk gathered in St. Petersburg in August 12th,2019 in a meeting where the sampling plan, the guidelines and some other sampling details and practices were discussed and agreed on.

The training, the guidance for sampling and the meetings ensured that the sampling staff was well prepared to the sampling. Some of the sampling equipment was not totally accordant with the recommendations. The recommendation of the test sampling before actual sampling did not take place. The fieldwork description as well as the deviations from the sampling plan are not reported in the 1st fieldwork report. Thus, the 1st fieldwork report is partly insufficient and does not serve the quality assurance process.

Eighteen quality control samples in total were taken in the first sampling phase. The amount of the quality control samples is according to recommendations. The analysis methods used for soil and sediment samples differs remarkably from the Finnish practices at least for metals. Thus, the metal concentrations in soil and sediment samples of the first sampling phase are not comparable to the Finnish guideline values nor the GTK results of the project standard. While the lead and mercury concentrations in the surface water blank sample were extremely high, the lead and mercury concentrations in the surface water samples of the 1st sampling phase should be considered only suggestive. More information about the Russian analysis methods for organic compounds is needed to ensure the comparability of the results to the Finnish guideline values. The Thompson-Howarth-plots of the soil, sediment and surface water sample pairs showed that in general, the precision of metal concentrations is not repeatable between routine and field duplicate samples. The LOI and pH values are repeatable in soil and sediment samples and the main anion and cation concentrations in surface water are repeatable. According to Thompson-Howarth-plots, the repeatability of pH analysis is very good while the precision of all the replicates is below 20 %. For the analysed metals, the analytical repeatability is good as well. Based on ANOVA, there was variation in concentrations of some substances depending on the sampling site or sampling layer. However, no statistical significance was found in duplicate or replicate samples. The variation was illustrated with boxplot diagrams to better detect the variation in concentrations between sites and inside the sampling layers as well.

Comparison between the detection limits of the Russian standard methods and the Finnish recommendations showed that Russian detection limits were higher than what is recommended in Finland for many substances, especially for stream water analyses. More sensitive analysis methods should be used in the next sampling round.

Uncertainty of measurements varied a lot between samples for some substances. Possible reasons for this could be asked from the laboratory.

9. Recommendations

The 1st sampling phase of the EnviTox project was well organized and successfully carried out by SC Mineral. However, there are some concerns and observations which will be good to take into account while the next sampling phases are planned in detailed.

The sampling plan has a significant role in each sampling phase and in the quality assurance process. Thus, it is important to pay attention to the planning of the sampling and keep the focus on the objectives of the project and the data and knowledge which are needed for to ensure the progress of the project. The main purpose of a sampling plan is to ensure the representativeness of the samples. It should include at least the aim of the study and sampling, the study and sampling area (maps, coordinates, coordinate system), sampling sites and sampling media/matrices, sampling dates, sampling techniques and sampling methods, information on field measurements, data collection and data storage practices, handling, transportation and storage of the samples, research and analysis methods, quality assurance, processing of the results and their reporting as well as the health and safety issues. The sampling plan will be delivered and presented to each person who attends to the sampling beforehand. This ensures that all the sampling staff is, in addition of the practical and technical issues, aware of the purpose of the sampling as well as the safety issues, and reports sampling in a consistent manner.

The sampling equipment and their use did not meet all the quality requirements. In order to avoid any cross-contamination due to sampling equipment, the surface water sampling and the sediment sampling should have their own scoops which are used only for its purpose. The scoops and buckets used in the sampling are recommended to be colourless and it would be practical to have at least two of them enclosed in case they got too dirty or are broken. It is suggested that the sample bottles of water samples for cation and metal analysis could be changed in colourless bottles with colourless caps. The origin of the high lead and mercury concentrations in the surface water blank sample could not be identified. In GTK, there are some experiences of the colourful caps having contaminated water samples, especially some metal concentrations detected in water samples have been due to the cap.

A fieldwork report (including all field sheets) should be written after the sampling campaign. This report describes the fieldwork and sampling work and observations made during the sampling. All deviations from the original sampling plan should be documented in the report.

The coming fieldwork and sampling campaigns will benefit if the quality control and assurance are further developed or improved. In general, the number of quality assurance samples (field duplicate and replicate samples) was adequate but it is necessary to increase the number of blank samples in surface water sample batches. It is recommended to take one blank sample in each surface water monitoring sampling tour. Depending on the number of the surface water samples during the next sampling stage, 1 blank sample / 10 samples should be included in the analysis batches. If the number of samples is less than 10, one blank sample should be included in each assay. In addition, it is suggested to consider whether a project standard or another kind of reference sample for organic compounds could be obtained and included in the analysis batches.

While exceptionally high concentrations of lead and mercury were detected from the blank sample, it is recommended to carry out a testing of the blank sample before the next sampling stage. This testing should be carried out by using similar sample bottle and cap as well as distilled water and acid as will be used at the next sampling stage. This is to ensure that these factors (bottle, cap and acid) do not cause any contamination in the water sample.

For the next sampling stages, it is recommended to pay a special attention to the analytical methods needed for the project purposes. Risk assessment tools and methods often requires information on both total and dissolved concentrations of contaminants. Thus, analytical methods should be chosen so that they meet the requirements of the Russian national standards but also risk assessment in general.

It is important to carefully clarify the limits of quantification in the analytical methods of laboratories. They should be in line with the national guidelines and be accurate enough to allow making comparisons to the national guideline and trigger values as well as risk assessment. Some reference analysis of each sampling matrix in another Russian accredited laboratory is compulsory in the coming sampling phases.

The pre-treatment of the soil and sediment samples for different analyses should be checked, paying special attention to drying, grounding, sieving, temperature and extraction methods. The samples should be dried in low temperature (usually < 40 °C) to avoid the evaporation of elements and compounds e.g. mercury. The samples for metal analysis should be ground, if needed, in a mill which does not cause any metal contamination, dry sieved in the required fraction size with a nylon sieve and no prewash for the soil and sediment samples is acceptable. The leaching methods for metal analysis of soil and sediment samples should be chosen by the data needs in the project (total, soluble, bioavailable etc. concentrations. For analysis of organic compounds, the analysis methods comparable to Finnish/ISO standard methods are recommended to use, if possible. The analysis report should explain the details of the conducted pre-treatment and extraction methods as well as analysis devices that have been used.

The provided excel files of the analysis results contained many typos which were detected in the statistical processing. The critical errors in the coordinates given in the result files caused a lot of extra work in the map production. Thus, the results of the next sampling stages should be received in digital format directly from the laboratory or at least the delivered result excel files should be double- or triple-checked before distributing for further interpretation.

All data, especially publicly available data should be accompanied by metadata documentation.

Relevant statistical analysis should be made not only for the data interpretation purposes but also for the preliminary quality checking.

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SOUTH-EAST FINLAND-RUSSIA CBC 2014-2020
KS 1203 Environmental impacts of the Krasny Bor toxic waste landfill (EnviTox)

Appendix 1

Thompson-Howarth plots of concentrations in soil, sediment and surface water field duplicate and replicate samples at the first sampling stage in the EnviTox project

GTK Open File Work Report 32/2020 GTK/73/03.01/2017

EnviTox – Quality Control of the First Fieldwork and Sampling Stage

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1. Thompson-Howarth plots of concentrations in soil field duplicate samples

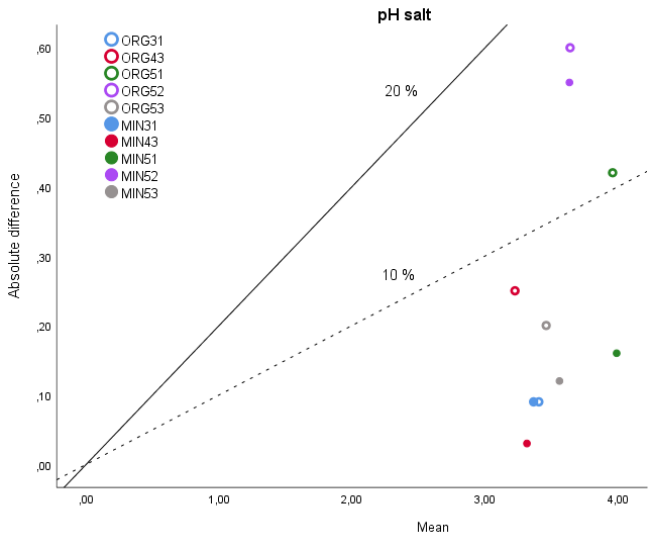

Figure 1.1. Thompson-Howarth -plot of pH values in soil in the 1st sampling phase of the EnviTox-project. The mean pH value of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm.

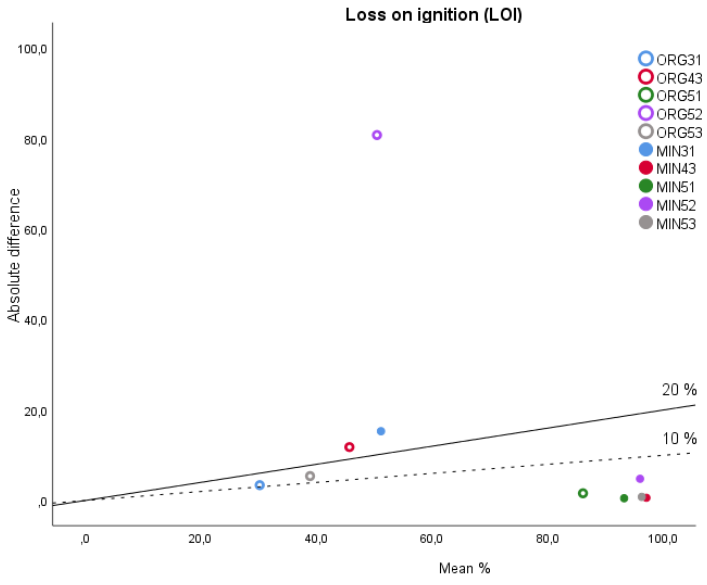

Figure 1.2. Thompson-Howarth -plot of Loss on Ignition (LOI) values in soil in the 1st sampling phase of the EnviTox-project. The mean LOI value of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm.

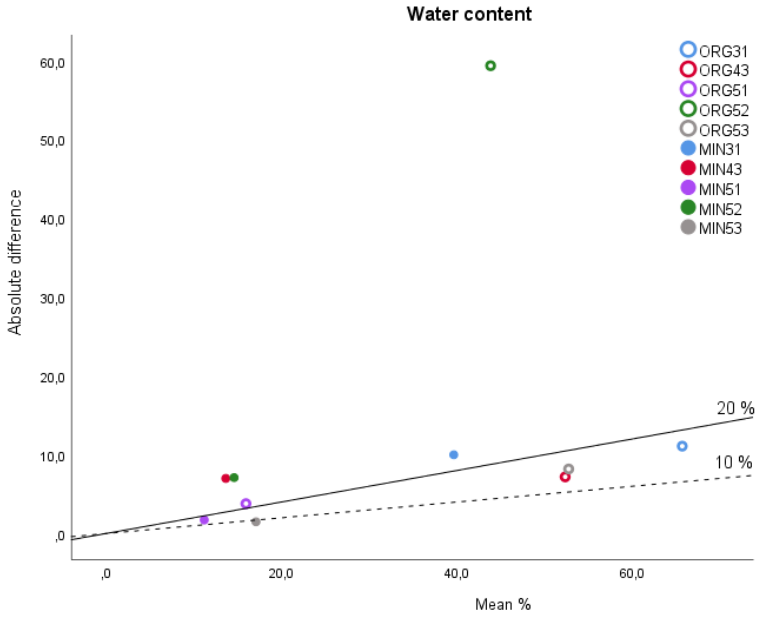

Figure 1.3. Thompson-Howarth-plot of water content in soil in the 1st sampling phase of the EnviTox-project. The mean water content of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm.

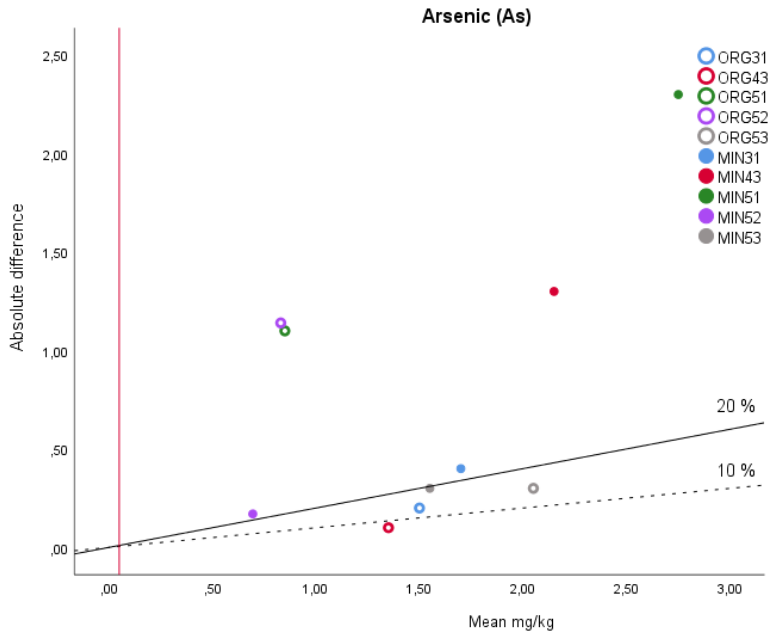

Figure 1.4. Thompson-Howarth-plot of As concentrations in soil in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean As concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. The red line = limit of quantification for As (0.05 mg/kg).

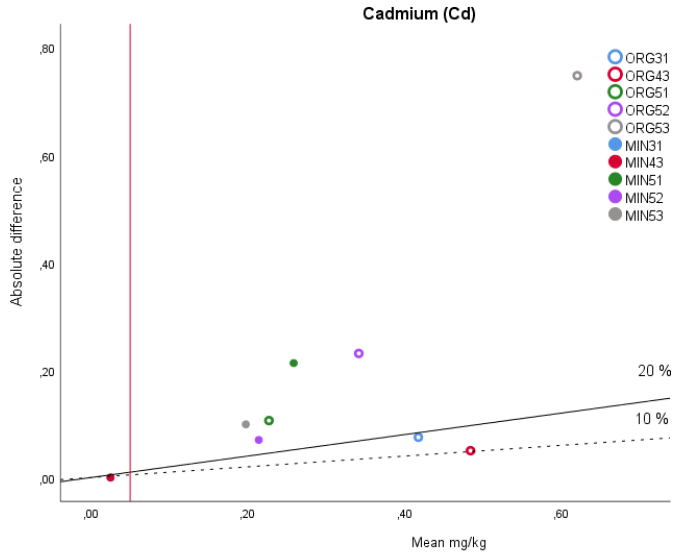

Figure 1.5. Thompson-Howarth-plot of Cd concentrations in soil in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean Cd concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. The red line = limit of quantification for Cd (0.05 mg/kg). In calculations, individual values with concentrations below the limit of quantification were converted to half of the limit of quantification. Thus, the sample pairs MIN31 and MIN43 appears below the limit of quantification line in the diagram.

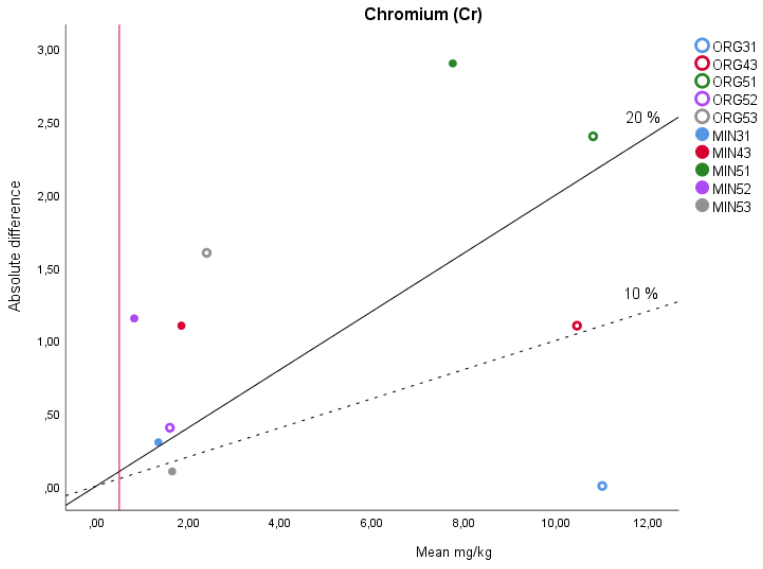

Figure 1.6. Thompson-Howarth-plot of Cr concentrations in soil in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean Cr concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. The red line = limit of quantification for Cr (0.5 mg/kg).

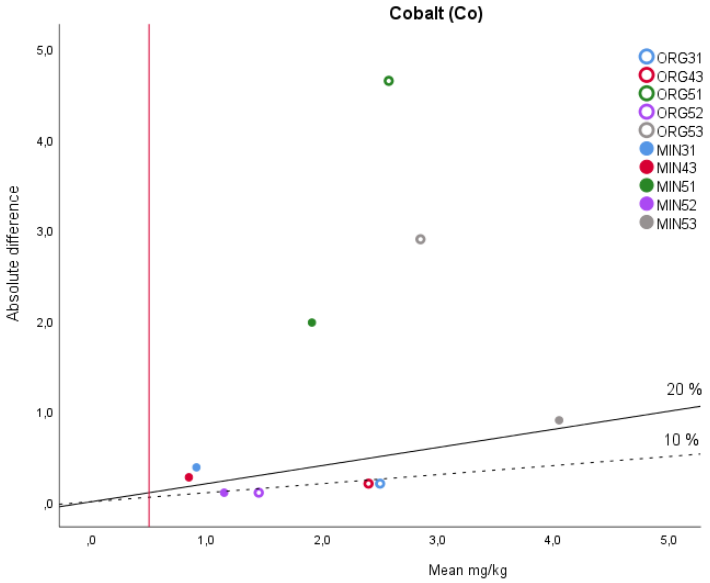

Figure 1.7. Thompson-Howarth-plot of Co concentrations in soil in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean Co concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. The red line = limit of quantification for Co (0.5 mg/kg).

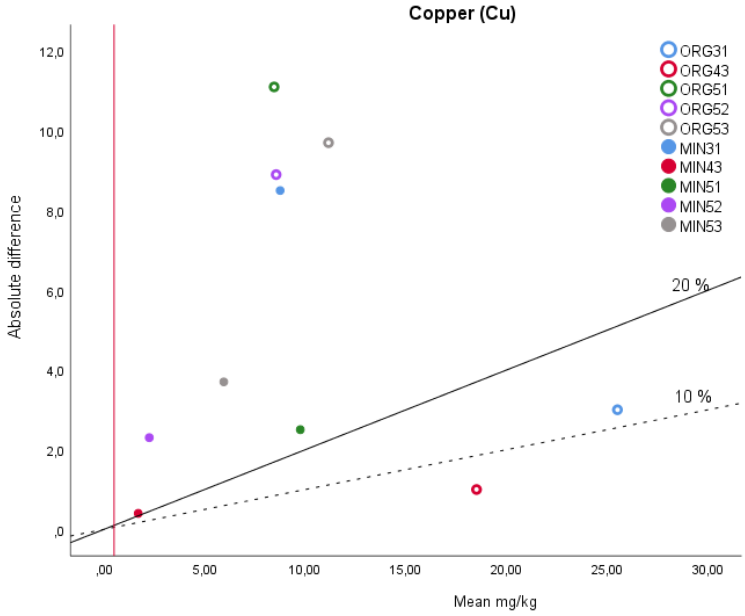

Figure 1.8. Thompson-Howarth-plot of Cu concentrations in soil in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean Cu concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. The red line = limit of quantification for Cu (0.5 mg/kg).

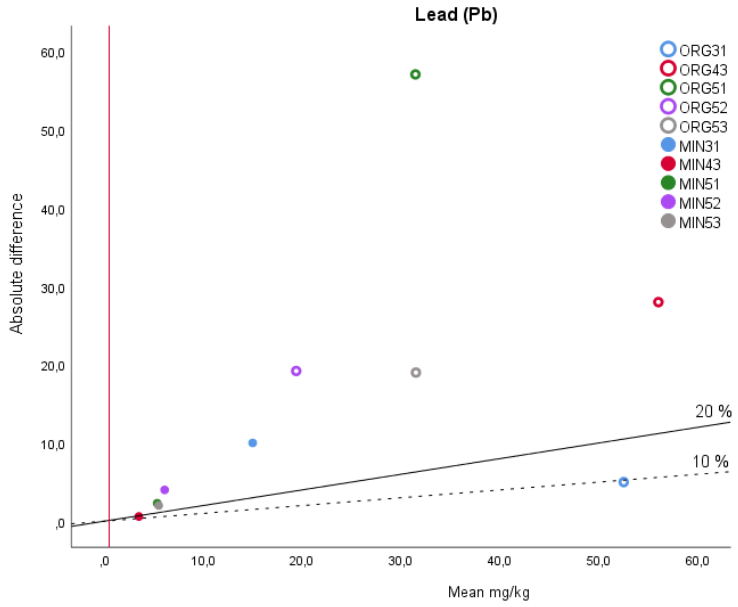

Figure 1.9. Thompson-Howarth-plot of Pb concentrations in soil in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean Pb concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. The red line = limit of quantification for Pb (0.5 mg/kg).

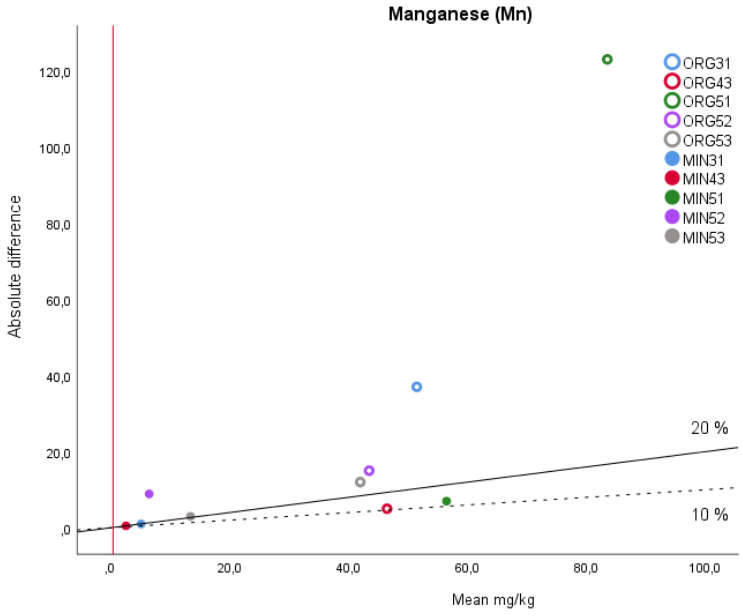

Figure 1.10. Thompson-Howarth-plot of Mn concentrations in soil in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean Mn concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. The red line = limit of quantification for Mn (0.5 mg/kg).

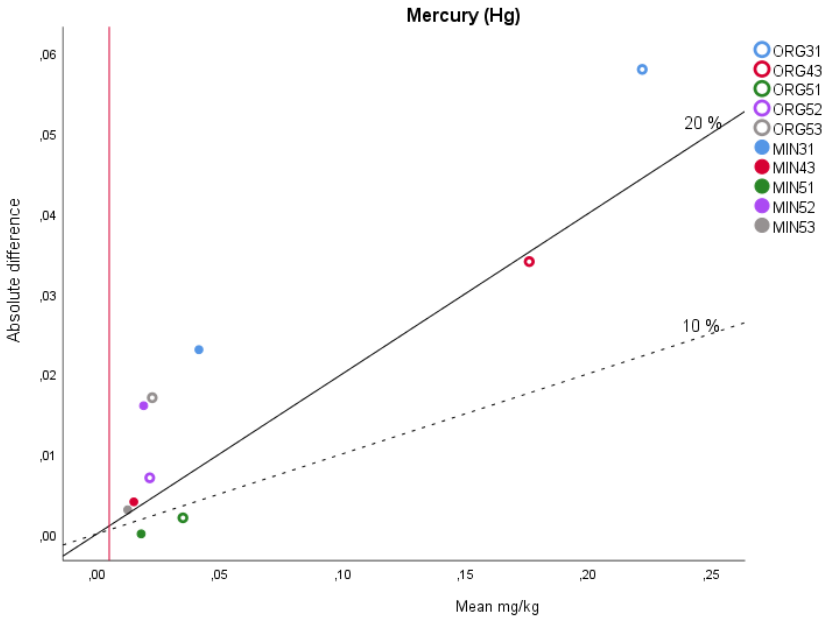

Figure 1.11. Thompson-Howarth-plot of Hg concentrations in soil in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean Hg concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. The red line = limit of quantification for Hg (0.005 mg/kg).

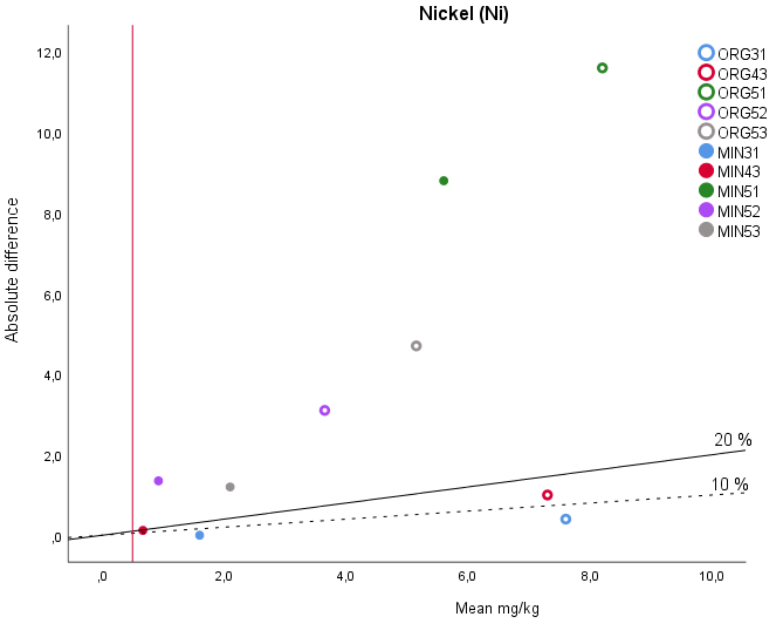

Figure 1.12. Thompson-Howarth-plot of Ni concentrations in soil in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean Ni concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. The red line = limit of quantification for Ni (0.5 mg/kg).

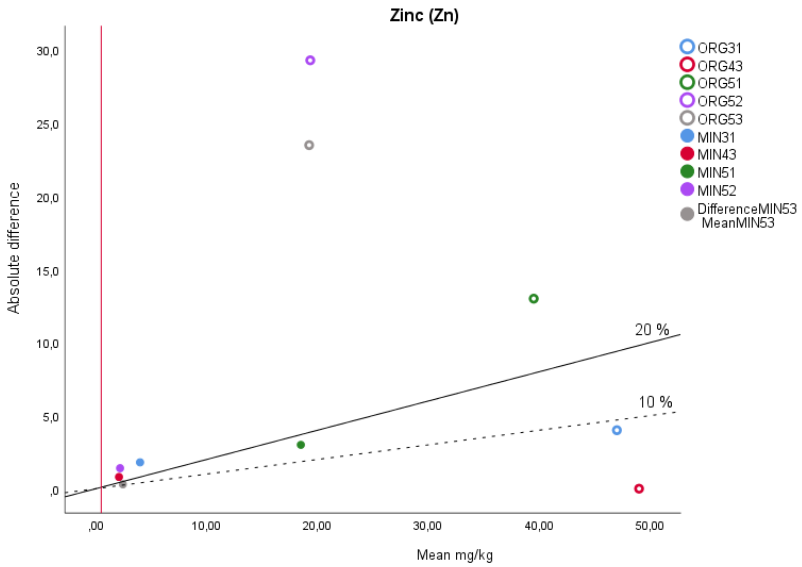

Figure 1.13. Thompson-Howarth-plot of Zn concentrations in soil in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean Zn concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. The red line = limit of quantification for Zn (0.5 mg/kg).

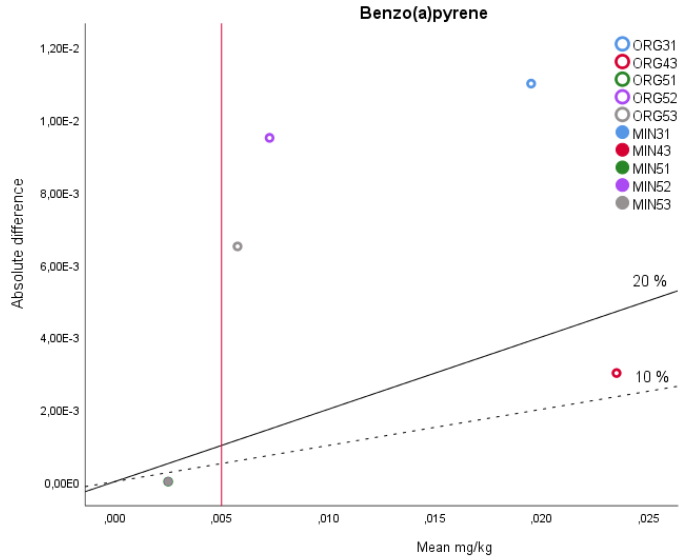

Figure 1.14. Thompson-Howarth-plot of benzo(a)pyrene concentrations in soil in the 1st sampling phase of the EnviTox-project. The mean benzo(a)pyrene concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. The red line = limit of quantification for benzo(a)pyrene (0.005 mg/kg). In calculations, individual values with concentrations below the limit of quantification were converted to half of the limit of quantification. Thus, the sample pair MIN53 appears below the limit of quantification line in the diagram. Only the plots of pairs with concentrations above the limit of quantification are shown in the diagram.

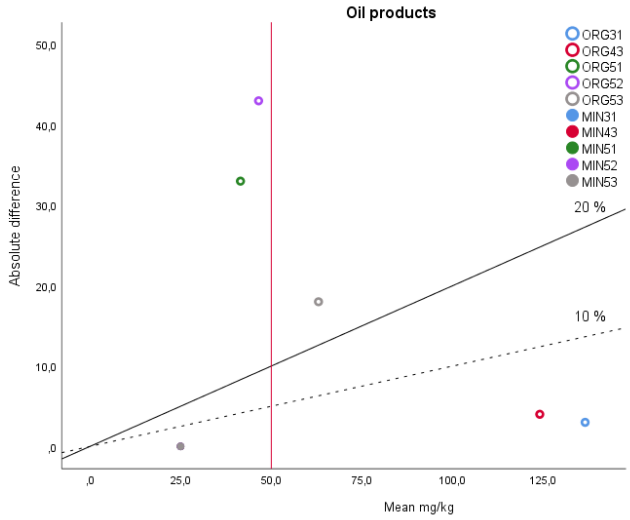

Figure 1.15. Thompson-Howarth-plot of oil product concentrations in soil in the 1st sampling phase of the EnviTox-project. The mean oil product concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. The red line = limit of quantification for oil products (50 mg/kg). In calculations, individual values with concentrations below the limit of quantification were converted to half of the limit of quantification. Thus, the sample pair MIN53 appears below the limit of quantification line in the diagram. Only the plots of pairs with concentrations above the limit of quantification are shown in the diagram.

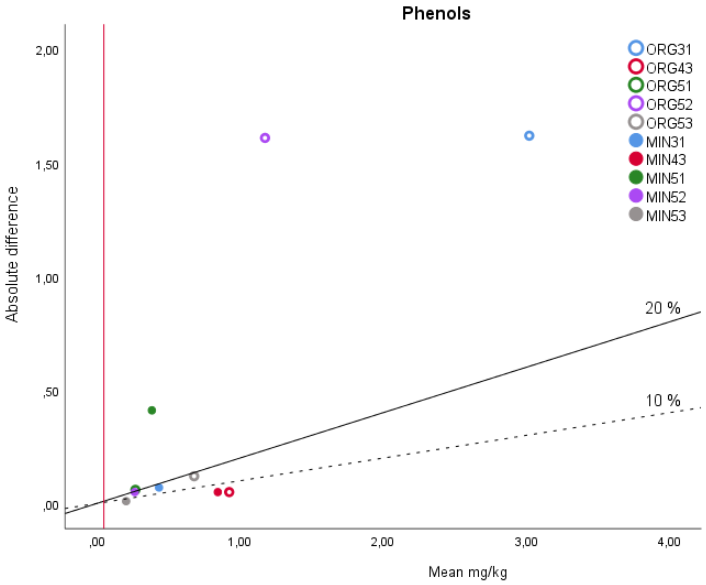

Figure 1.16. Thompson-Howarth-plot of phenol concentrations in soil in the 1st sampling phase of the EnviTox-project. The mean phenol concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. The red line = limit of quantification for phenols (0.05 mg/kg).

2. Thompson-Howarth plots of concentrations in soil replicate samples

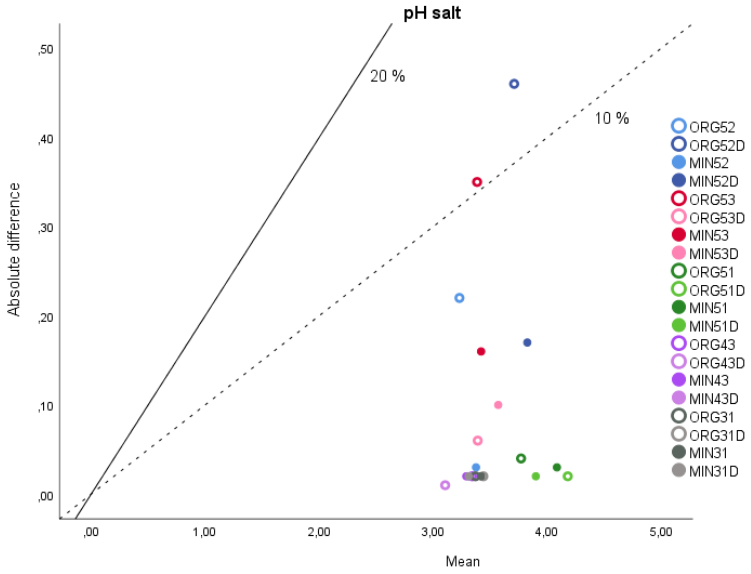

Figure 2.1. Thompson-Howarth-plot of pH values in soil replicate samples in the 1st sampling phase of the EnviTox-project. The mean pH value of the routine and the repeated measurement in each sample pair is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. Sample with 'D' in the sample code is the field duplicate sample of the sample with the same number.

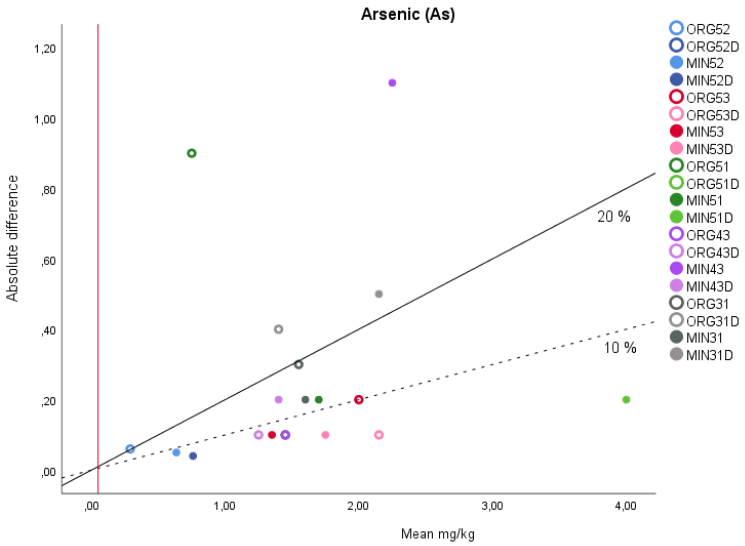

Figure 2.2. Thompson-Howarth-plot of As concentrations in soil replicate samples in the 1st sampling phase of the EnviTox-project (< 1 mm, grain size, 5 M HNO_3 extraction). The mean As concentration of the routine and repeated analysis is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. Sample with 'D' in the sample code is the field duplicate sample of the sample with the same number. The red line = limit of quantification for As (0.05 mg/kg).

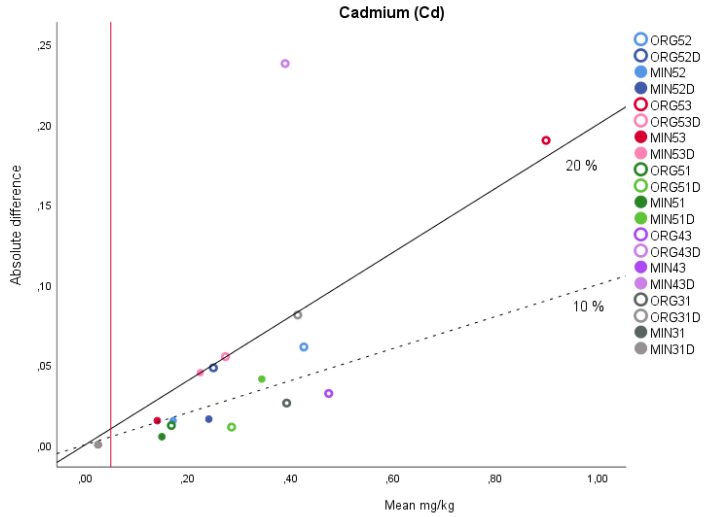

Figure 2.3. Thompson-Howarth-plot of Cd concentrations in soil replicate samples in the 1st sampling phase of the EnviTox-project (< 1 mm, grain size, 5 M HNO_3 extraction). The mean Cd concentration of the routine and repeated analysis is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. Sample with 'D' in the sample code is the field duplicate sample of the sample with the same number. The red line = limit of quantification for Cd (0.05 mg/kg). In calculations, individual values with concentrations below the limit of quantification were converted to half of the limit of quantification. Thus, the sample pair MIN31D appears below the limit of quantification line in the diagram.

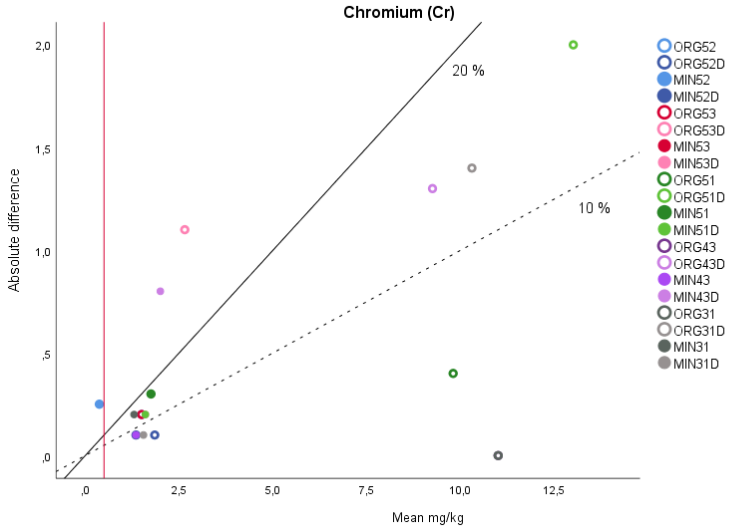

Figure 2.4. Thompson-Howarth-plot of Cr concentrations in soil replicate samples in the 1st sampling phase of the EnviTox-project (< 1 mm, grain size, 5 M HNO_3 extraction). The mean Cr concentration of the routine and repeated analysis is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. Sample with 'D' in the sample code is the field duplicate sample of the sample with the same number. The red line = limit of quantification for Cr (0.5 mg/kg). In calculations, individual values with concentrations below the limit of quantification were converted to half of the limit of quantification. Thus, the sample pair MIN52 appears below the limit of quantification line in the diagram.

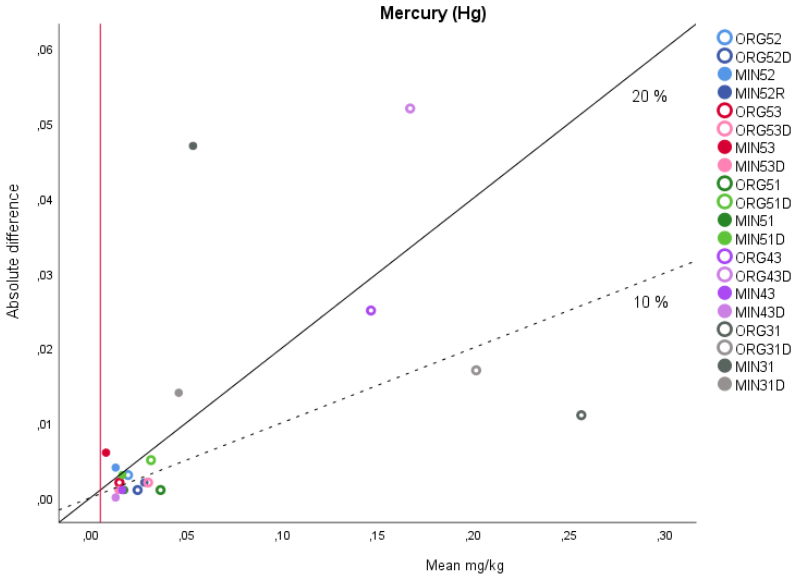

Figure 2.5. Thompson-Howarth-plot of Hg concentrations in soil replicate samples in the 1st sampling phase of the EnviTox-project (< 1 mm, grain size, 5 M HNO_3 extraction). The mean Hg concentrations of the routine and repeated analysis is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. Sample with 'D' in the sample code is the field duplicate sample of the sample with the same number. The red line = limit of quantification for Hg (0.005 mg/kg).

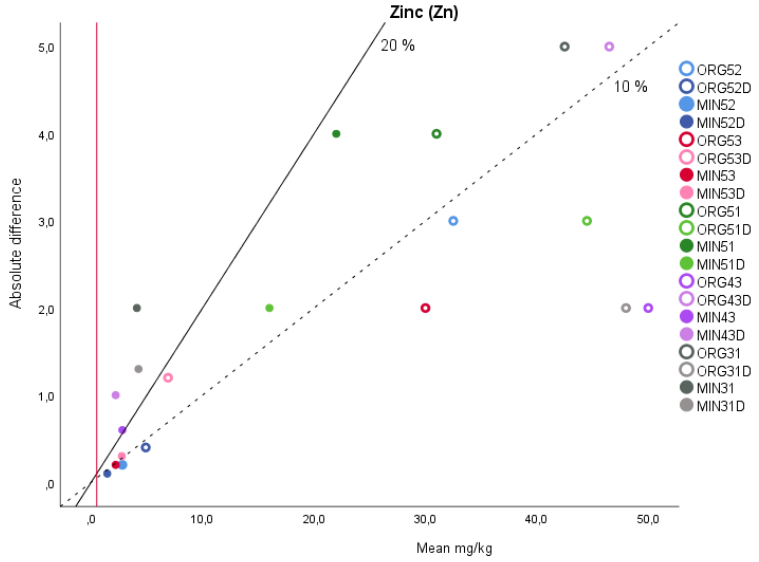

Figure 2.6. Thompson-Howarth-plot of Zn concentrations in soil replicate samples in the 1st sampling phase of the EnviTox-project (< 1 mm, grain size, 5 M HNO_3 extraction). The mean Zn concentrations of the routine and repeated analysis is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. Sample with 'D' in the sample code is the field duplicate sample of the sample with the same number. The red line = limit of quantification for Zn (0.5 mg/kg).

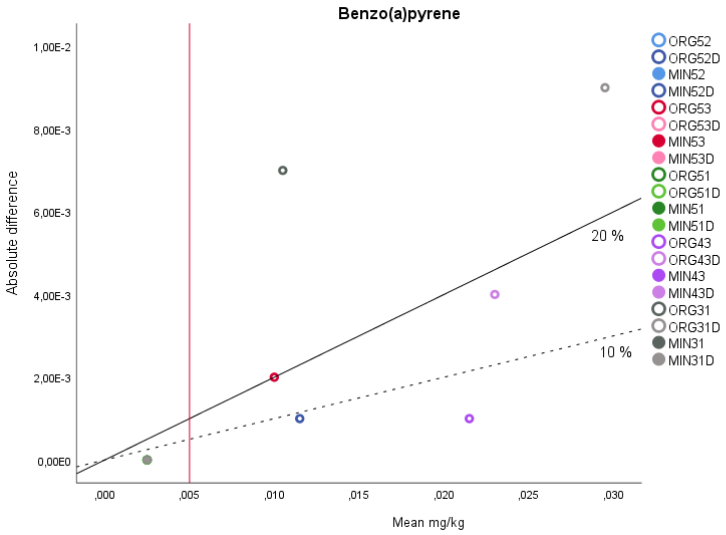

Figure 2.7. Thompson-Howarth-plot of benzo(a)pyrene concentrations in soil replicate samples in the 1st sampling phase of the EnviTox-project. The mean benzo(a)pyrene concentrations of the routine and repeated analysis is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. ORG = sampling depth 0 – 5 cm, MIN= sampling depth 5 – 20 cm. Sample with 'D' in the sample code is the field duplicate sample of the sample with the same number. The red line = limit of quantification for benzo(a)pyrene (0.005 mg/kg). In calculations, individual values with concentrations below the limit of quantification were converted to half of the limit of quantification. Thus, the sample pair MIN31D appears below the limit of quantification line in the diagram. Only the plots of pairs with concentrations above the limit of quantification are shown in the diagram.

3. Thompson-Howarth plots of concentrations in sediment field duplicate samples

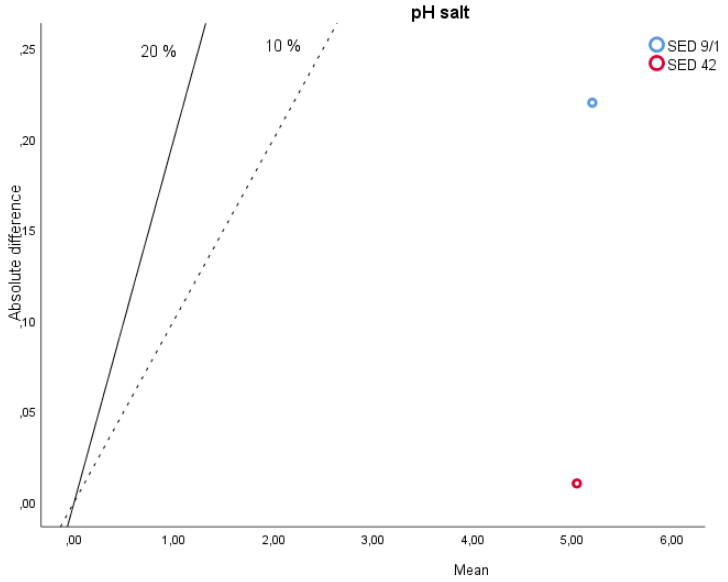

Figure 3.1. Thompson-Howarth -plot of pH values in sediment in the 1st sampling phase of the EnviTox-project. The mean pH value of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis.

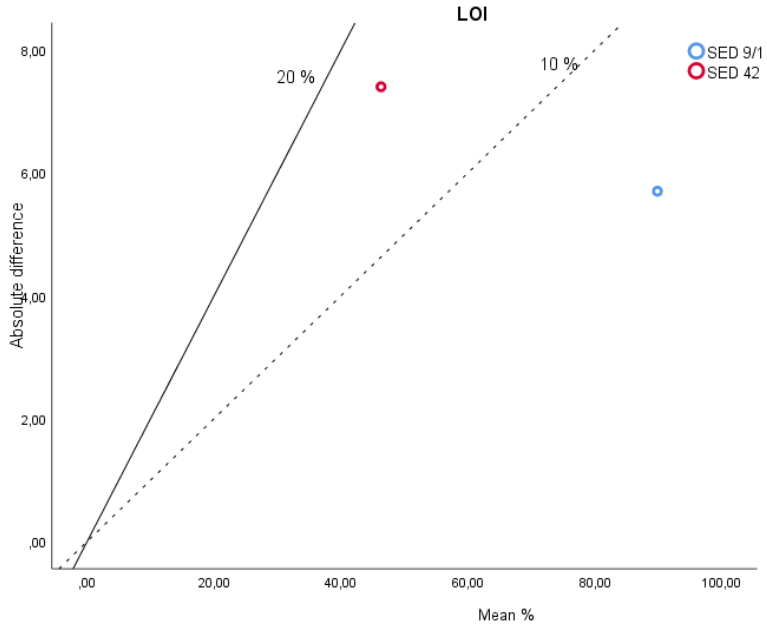

Figure 3.2. Thompson-Howarth -plot of Loss on Ignition (LOI) values in sediment in the 1st sampling phase of the EnviTox-project. The mean LOI value of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis.

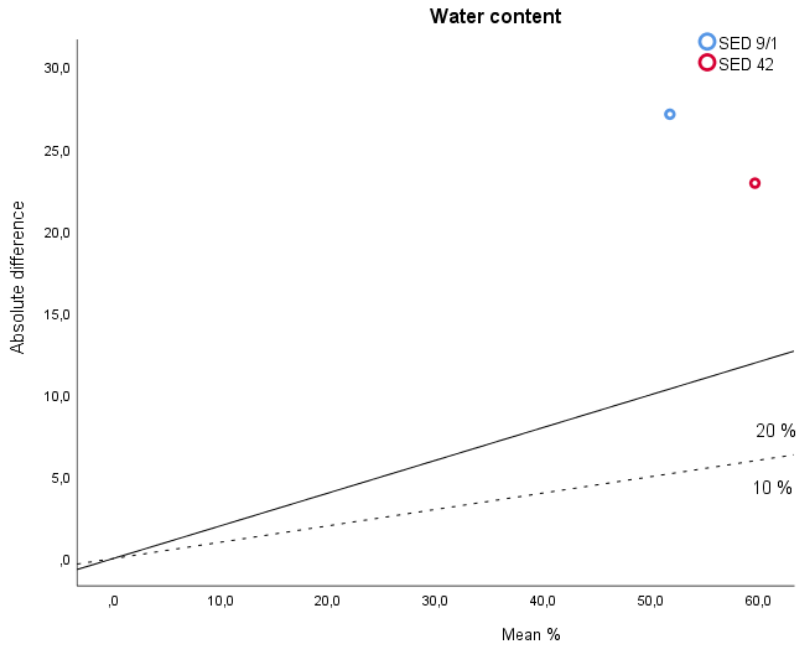

Figure 3.3. Thompson-Howarth-plot of water content in sediment in the 1st sampling phase of the EnviTox-project. The mean water content of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis.

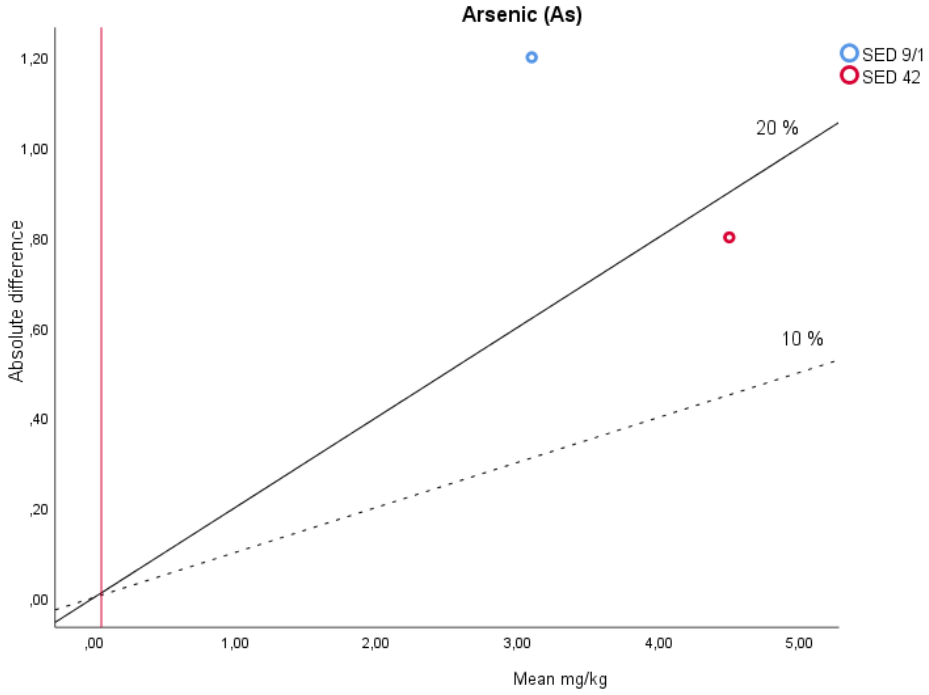

Figure 3.4. Thompson-Howarth-plot of As concentrations in sediment in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean As concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for As (0.05 mg/kg).

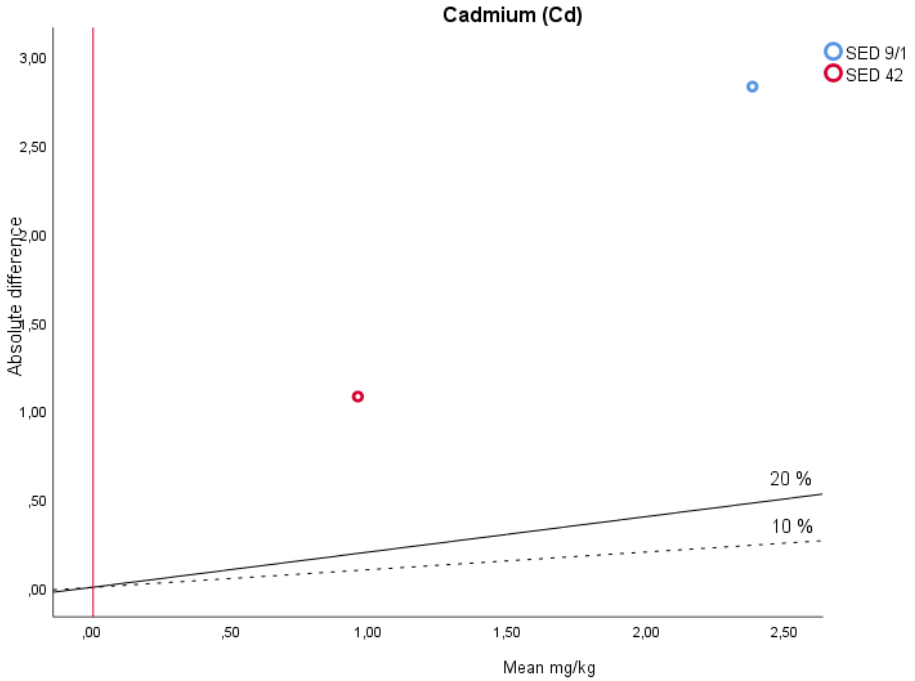

Figure 3.5. Thompson-Howarth-plot of Cd concentrations in sediment in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean Cd concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for Cd (0.05 mg/kg).

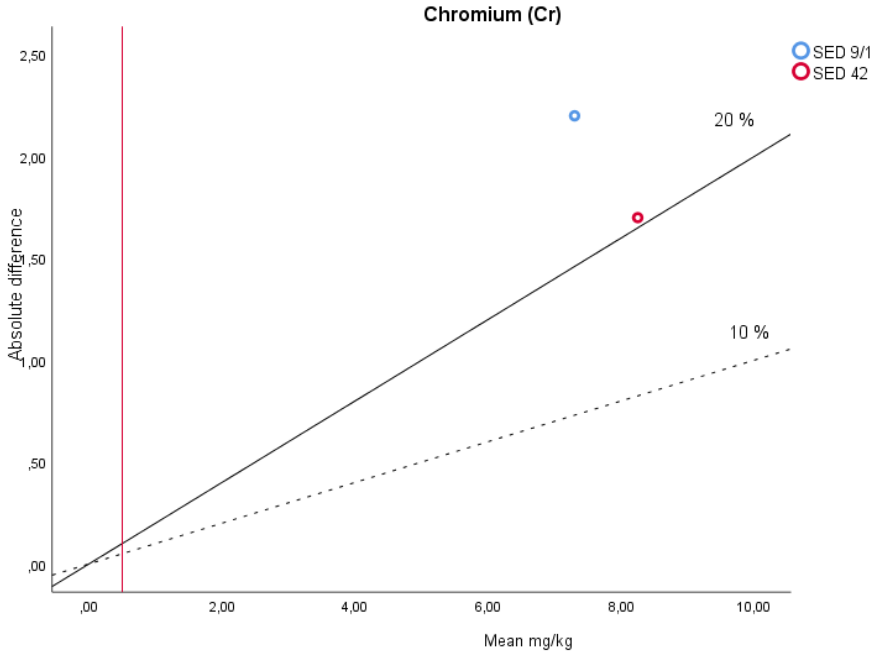

Figure 3.6. Thompson-Howarth-plot of Cr concentrations in sediment in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean Cr concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for Cr (0.5 mg/kg).

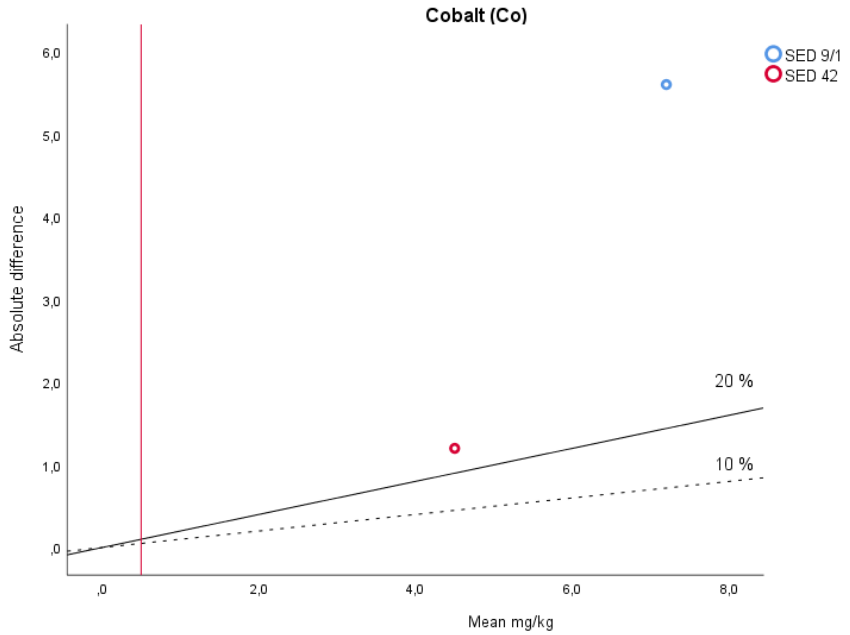

Figure 3.7. Thompson-Howarth-plot of Co concentrations in sediment in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean Co concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for Co (0.5 mg/kg).

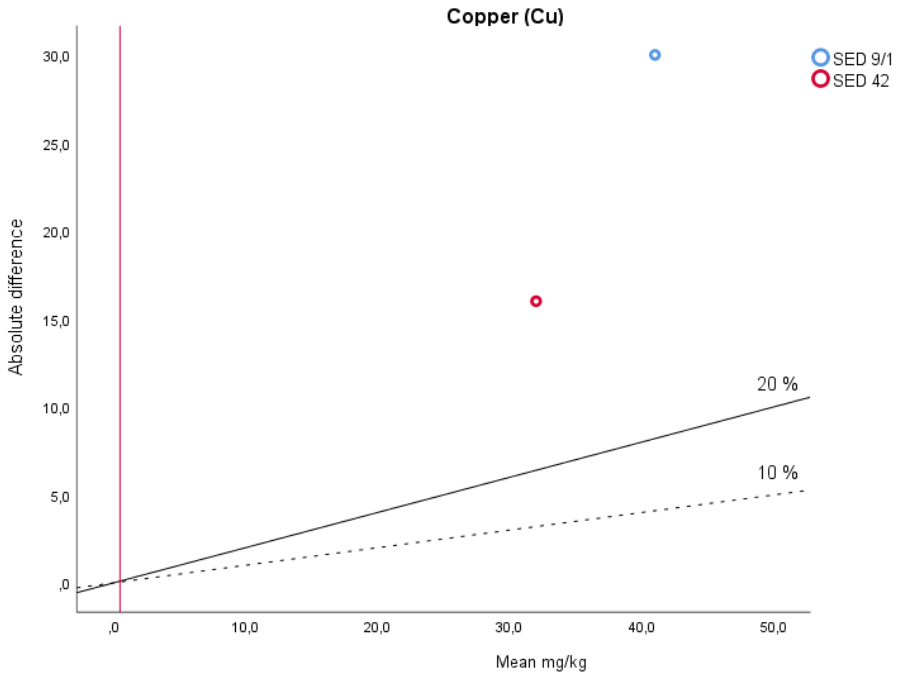

Figure 3.8. Thompson-Howarth-plot of Cu concentrations in sediment in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean Cu concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for Cu (0.5 mg/kg).

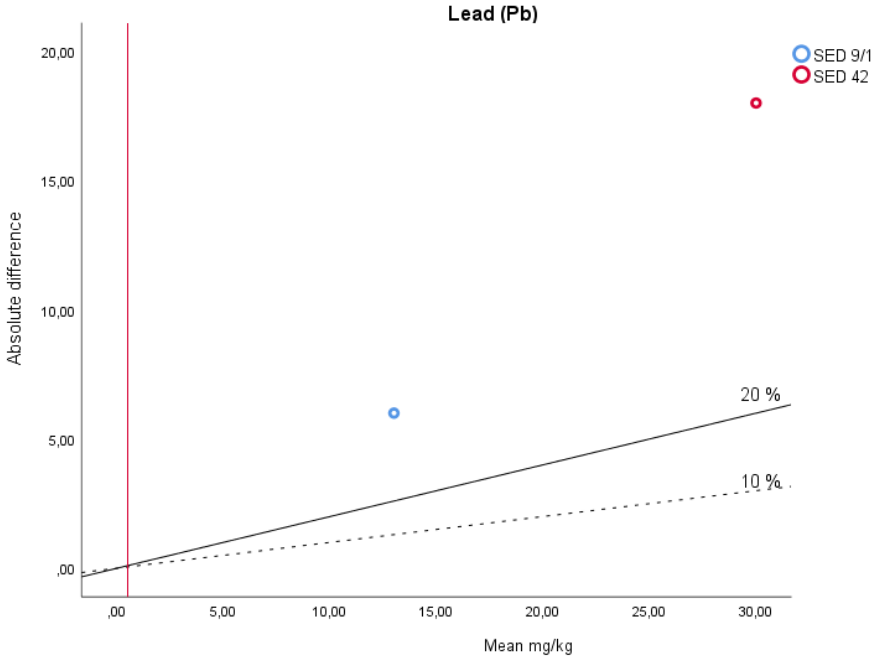

Figure 3.9. Thompson-Howarth-plot of Pb concentrations in sediment in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean Pb concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for Pb (0.5 mg/kg).

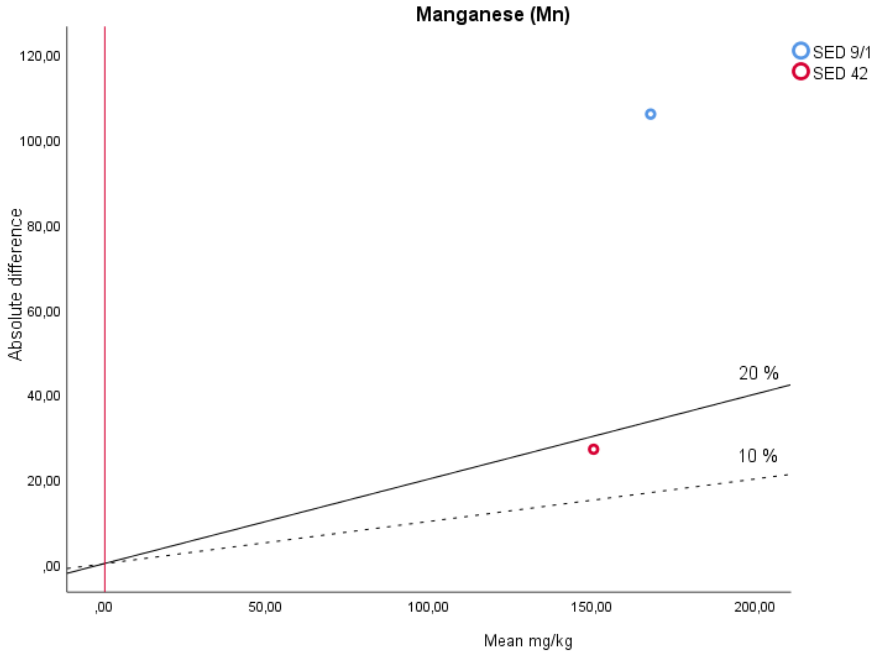

Figure 3.10. Thompson-Howarth-plot of Mn concentrations in sediment in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean Mn concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for Mn (0.5 mg/kg).

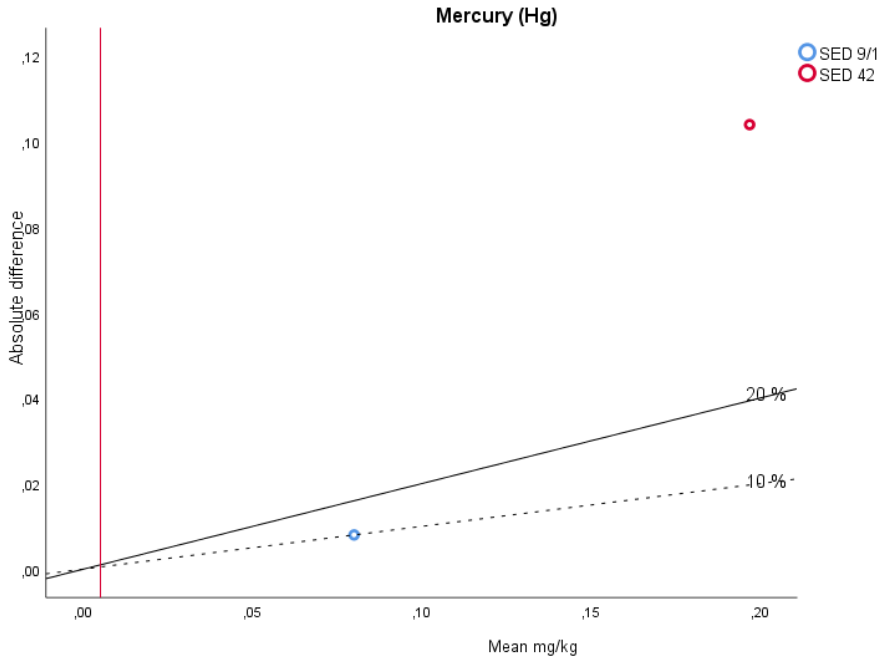

Figure 3.11. Thompson-Howarth-plot of Hg concentrations in sediment in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean Hg concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for Hg (0.005 mg/kg).

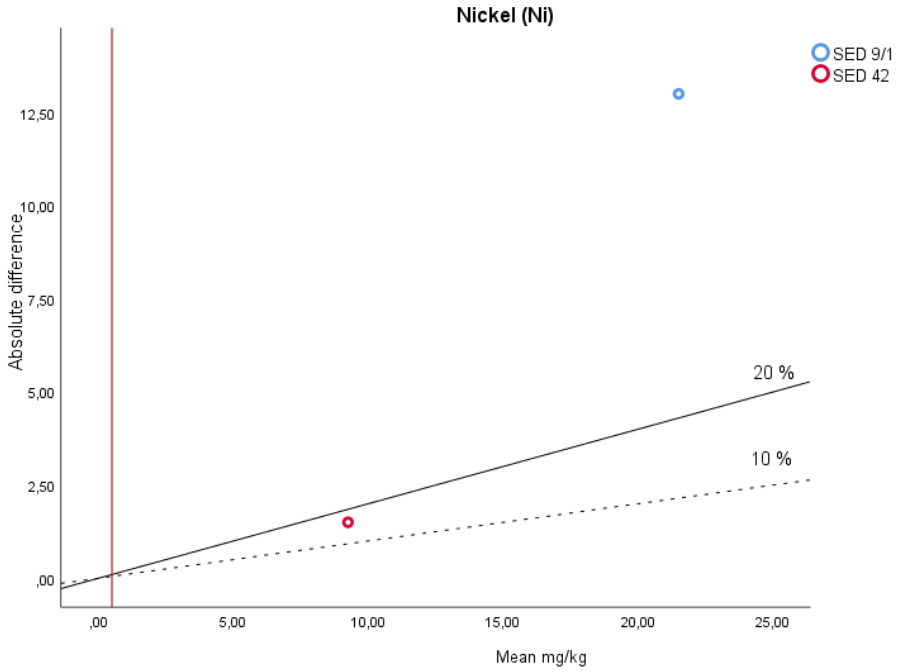

Figure 3.12. Thompson-Howarth-plot of Ni concentrations in sediment in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean Ni concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for Ni (0.5 mg/kg).

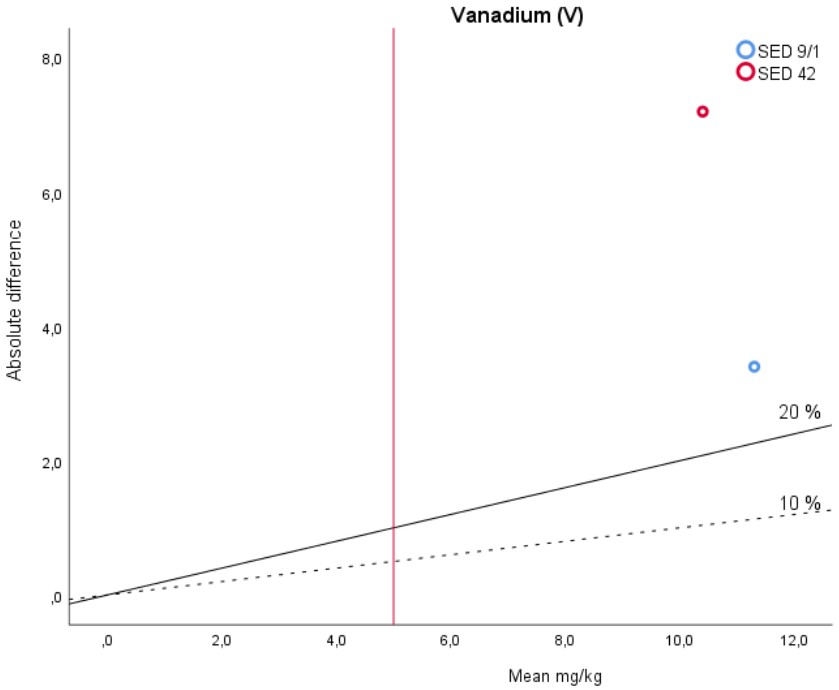

Figure 3.13. Thompson-Howarth-plot of V concentrations in sediment in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean V concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for V (5 mg/kg).

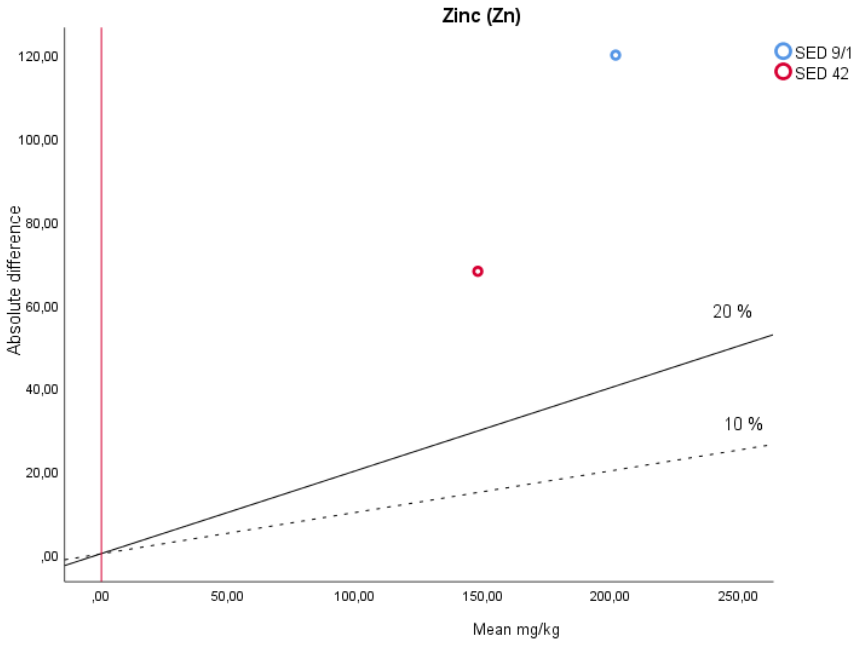

Figure 3.14. Thompson-Howarth-plot of Zn concentrations in sediment in the 1st sampling phase of the EnviTox-project (< 1 mm grain size, 5M HNO_3 extraction). The mean Zn concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for Zn (0.5 mg/kg).

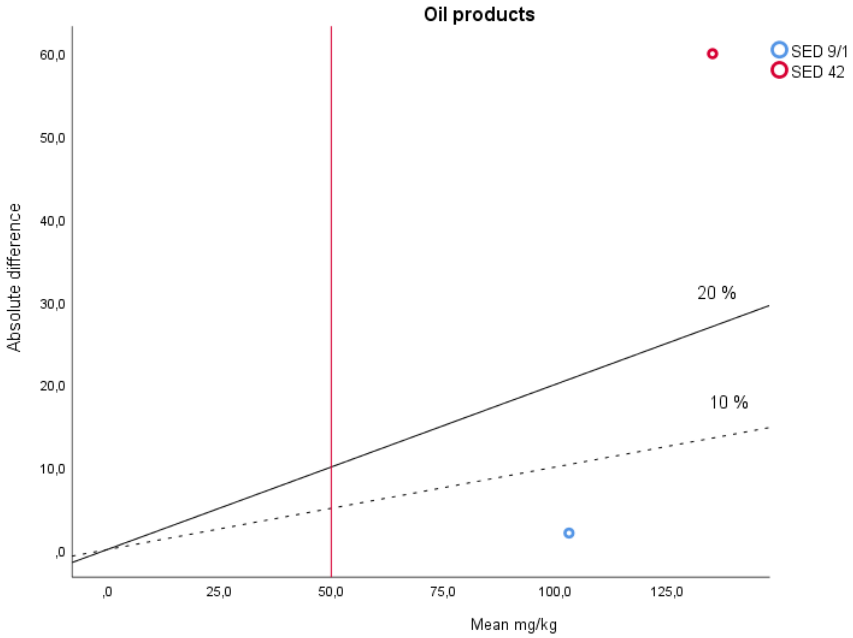

Figure 3.15. Thompson-Howarth-plot of oil product concentrations in sediment in the 1st sampling phase of the EnviTox-project. The mean oil product concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for oil products (50 mg/kg).

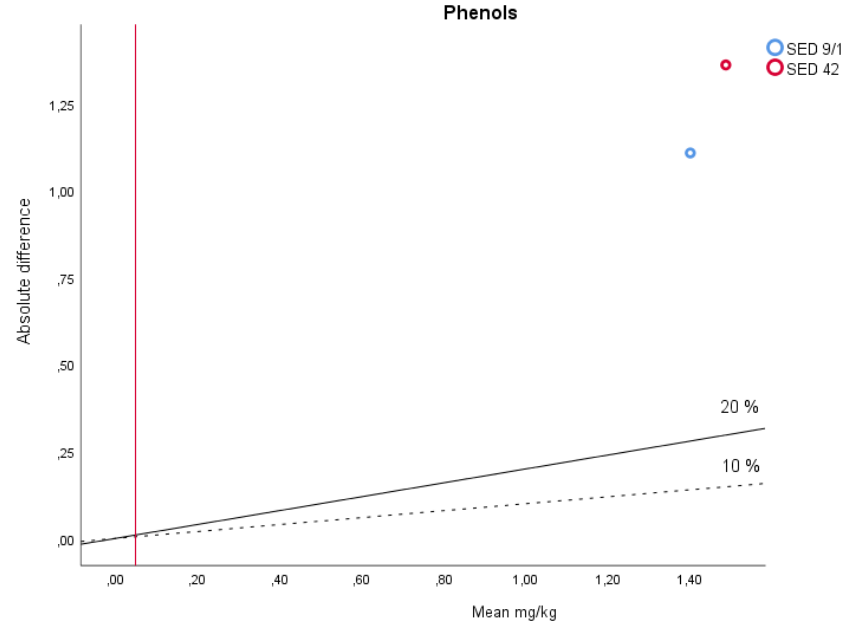

Figure 3.16. Thompson-Howarth-plot of phenol concentrations in sediment in the 1st sampling phase of the EnviTox-project. The mean phenol concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for phenols (0.05 mg/kg).

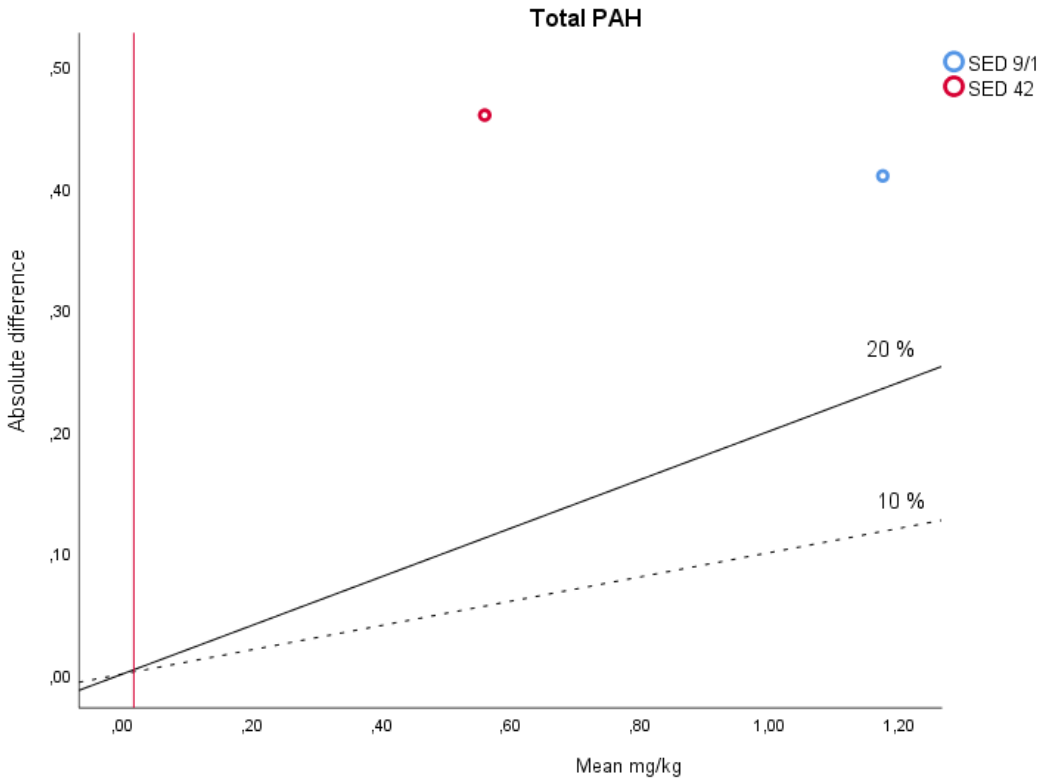

Figure 3.17. Thompson-Howarth-plot of total PAH concentrations in sediment in the 1st sampling phase of the EnviTox-project. The mean total PAH concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for total PAH (0.005 mg/kg).

4. Thompson-Howarth plots of concentrations in surface water field duplicate samples

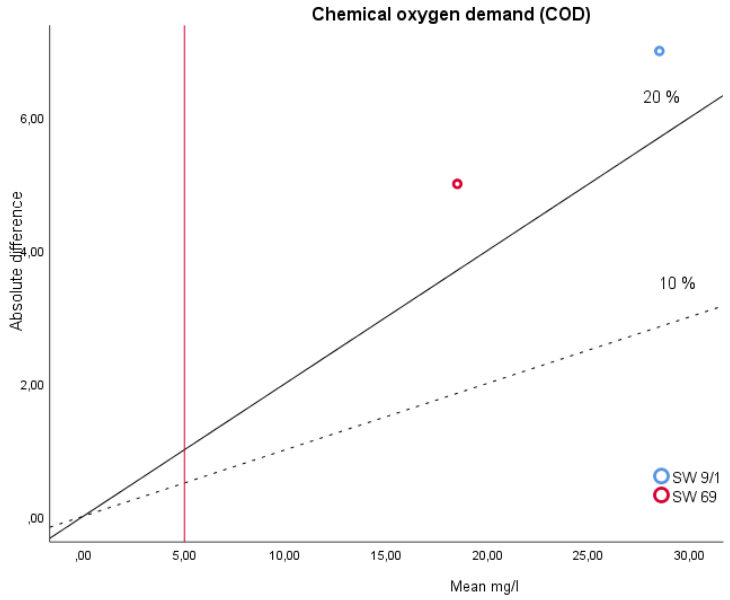

Figure 4.1. Thompson-Howarth-plot of COD values in surface water in the 1st sampling phase of the EnviTox-project. The mean COD value of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for COD (5 mg/kg).

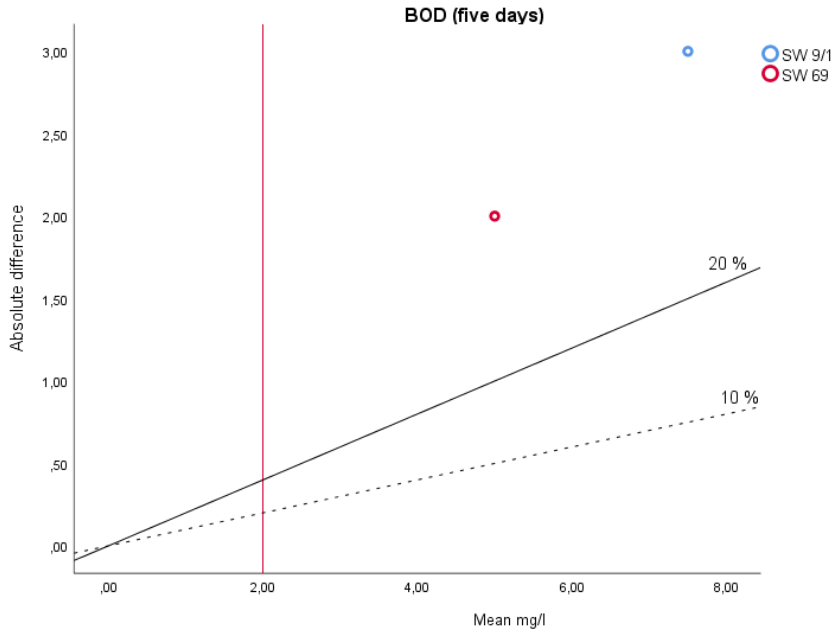

Figure 4.2. Thompson-Howarth-plot of BOD (five days) values in surface water in the 1st sampling phase of the EnviTox-project. The mean BOD (five days) value of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for BOD (five days) (2 mg/kg).

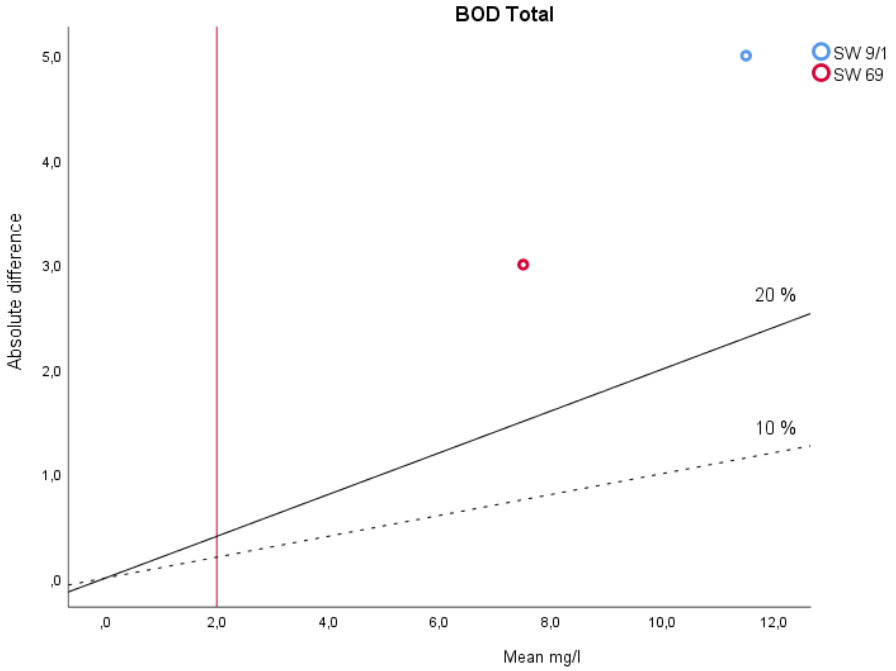

Figure 4.3. Thompson-Howarth-plot of BOD total values in surface water in the 1st sampling phase of the EnviTox-project. The mean BOD total value of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for BOD total (2 mg/kg).

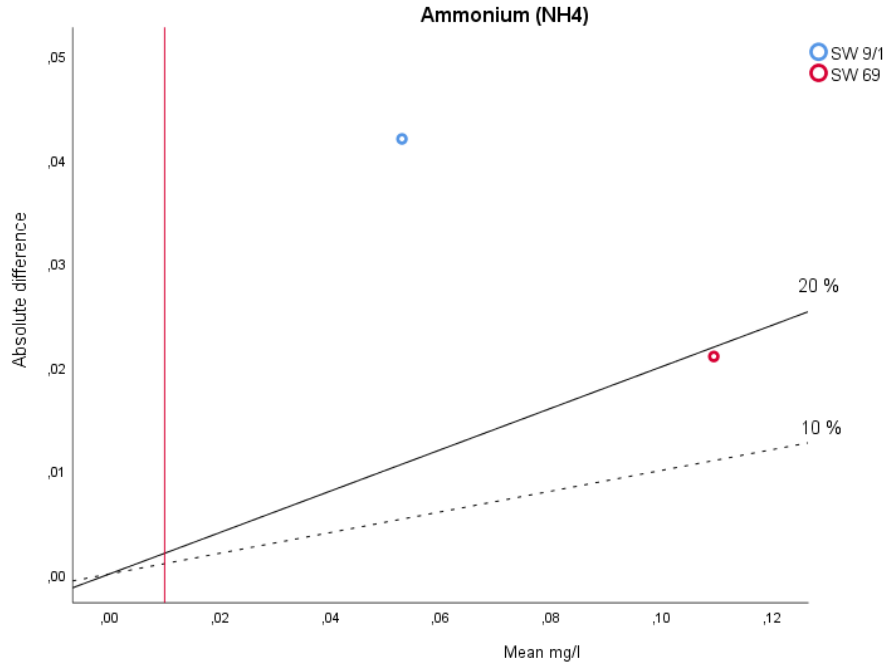

Figure 4.4. Thompson-Howarth-plot of NH_4 concentrations in surface water in the 1st sampling phase of the EnviTox-project. The mean NH_4 of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for NH_4 (0.01 mg/kg).

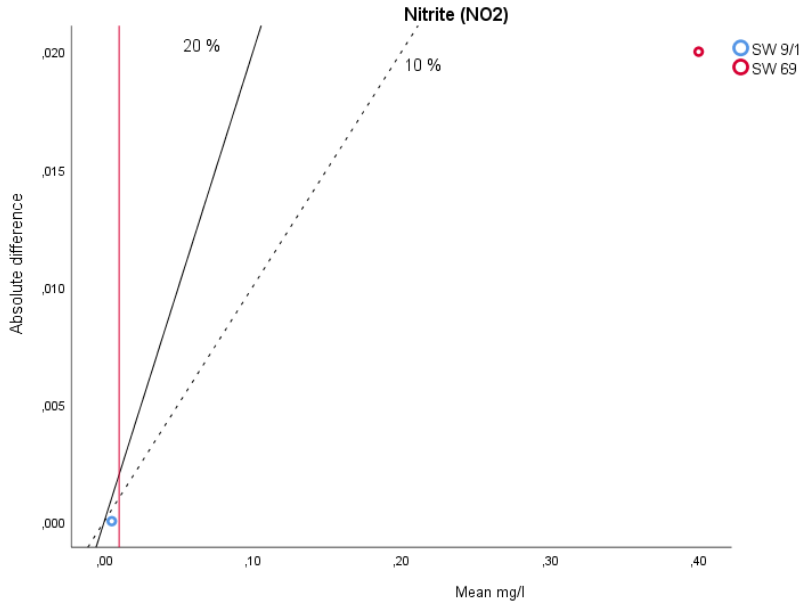

Figure 4.5. Thompson-Howarth-plot of NO_2 concentrations in surface water in the 1st sampling phase of the EnviTox-project. The mean NO_2 of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for NO_2 (0.01 mg/kg). In calculations, individual values with concentrations below the limit of quantification were converted to half of the limit of quantification. Thus, the sample pair SW 9/1 appears below the limit of quantification line in the diagram.

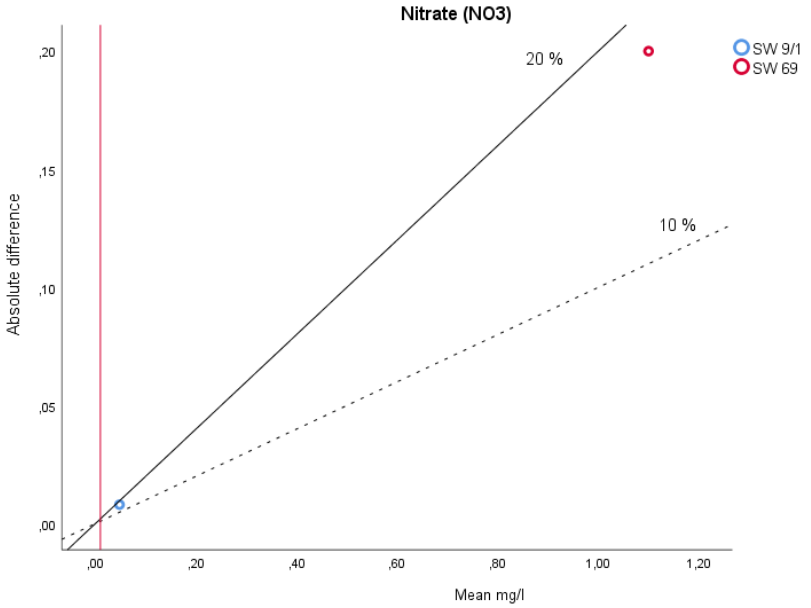

Figure 4.6. Thompson-Howarth-plot of NO_3 concentrations in surface water in the 1st sampling phase of the EnviTox-project. The mean NO_3 of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for NO_3 (0.01 mg/kg).

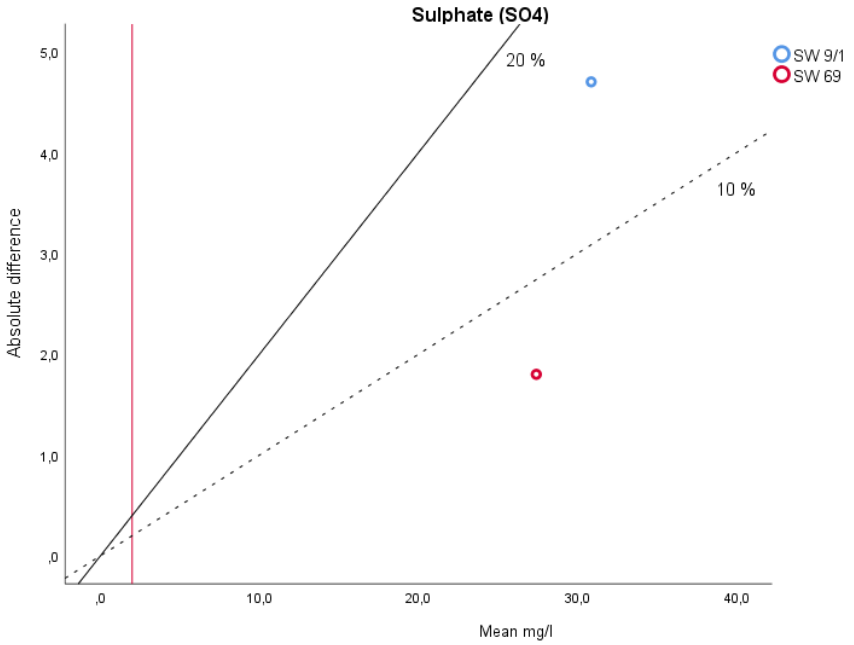

Figure 4.7. Thompson-Howarth-plot of SO_4 concentrations in surface water in the 1st sampling phase of the EnviTox-project. The mean SO_4 of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for SO_4 (5 mg/kg).

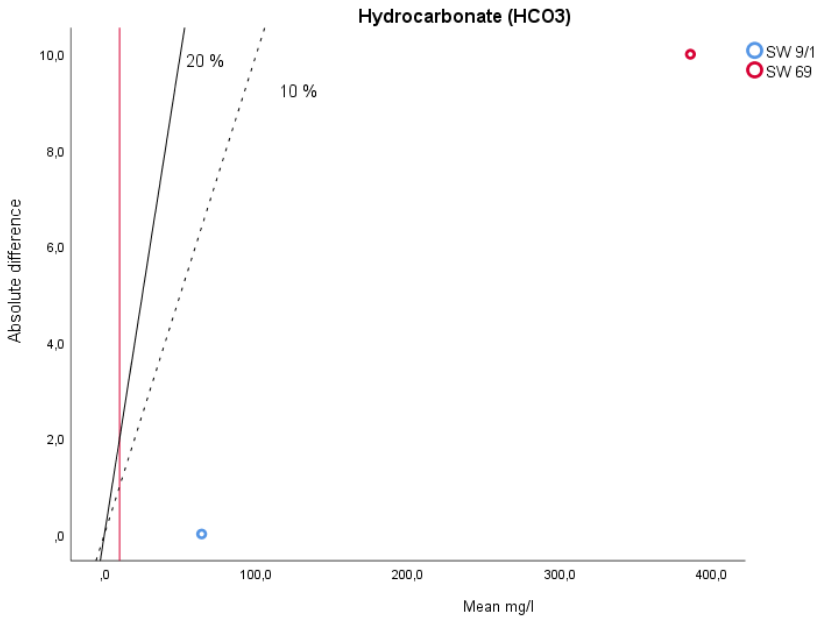

Figure 4.8. Thompson-Howarth-plot of HCO_3 concentrations in surface water in the 1st sampling phase of the EnviTox-project. The mean HCO_3 of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for HCO_3 (10 mg/kg).

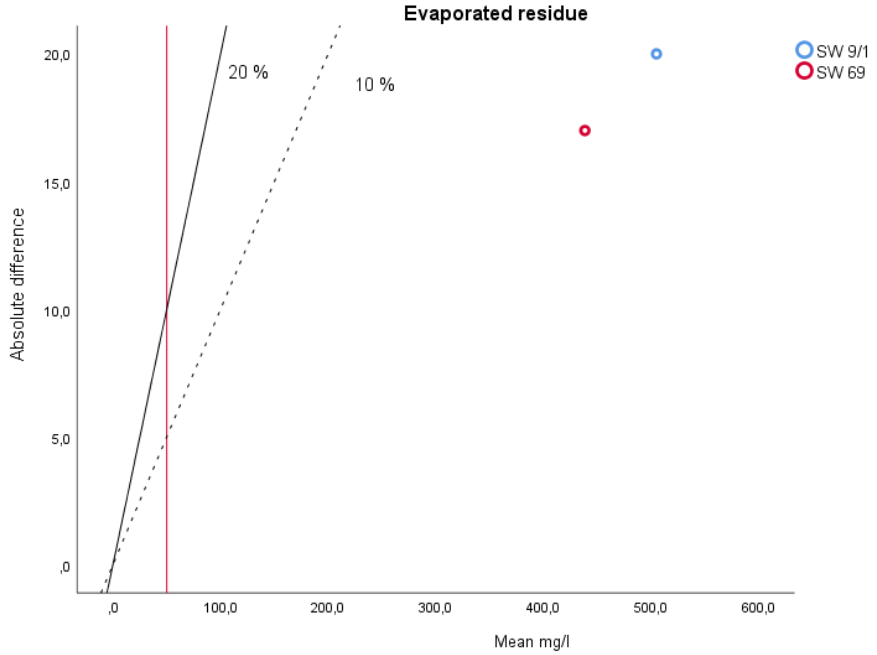

Figure 4.9. Thompson-Howarth-plot of evaporated residue values in surface water in the 1st sampling phase of the EnviTox-project. The mean evaporated residue values of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for evaporated residue (50 mg/kg).

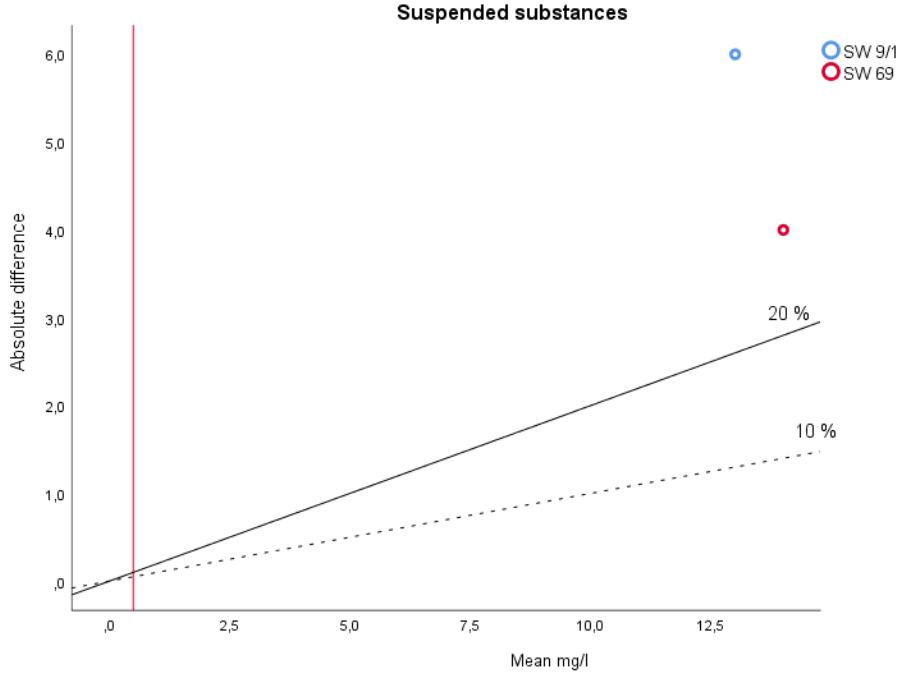

Figure 4.10. Thompson-Howarth-plot of suspended substances values in surface water in the 1st sampling phase of the EnviTox-project. The mean suspended substances values of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for suspended substances (0.5 mg/kg).

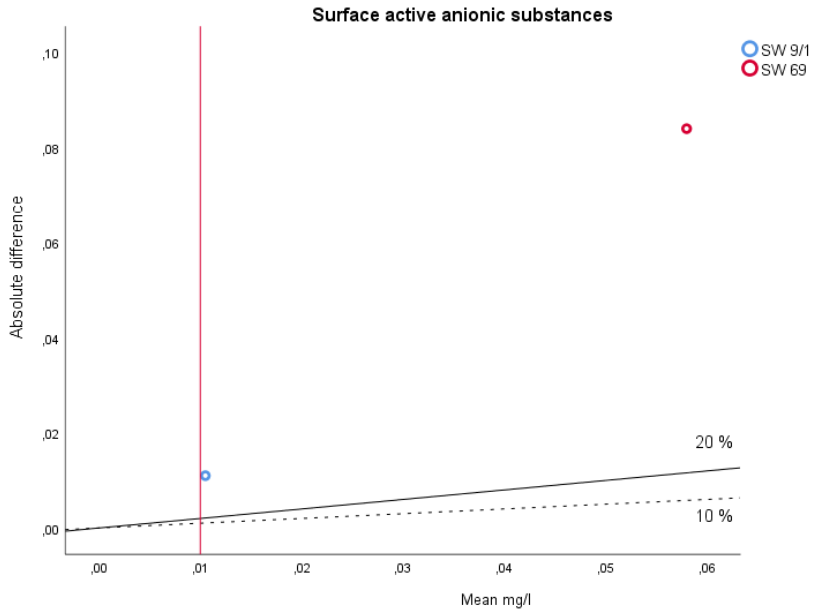

Figure 4.11. Thompson-Howarth-plot of surface active anionic substances in surface water in the 1st sampling phase of the EnviTox-project. The mean of surface active anionic substances of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for of surface active anionic substances (0.01 mg/kg).

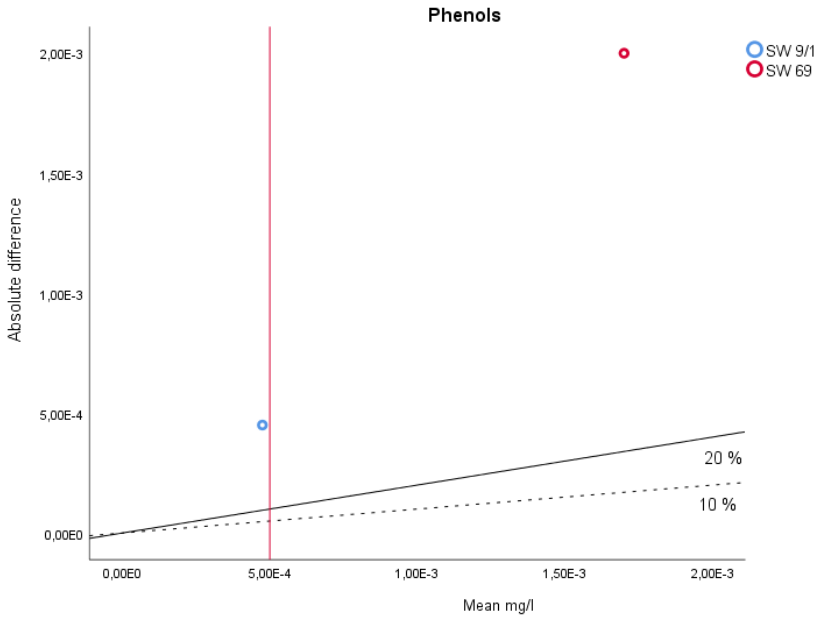

Figure 4.12. Thompson-Howarth-plot of phenols in surface water in the 1st sampling phase of the EnviTox-project. The mean of phenols of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for of phenols (0.0005 mg/kg). In calculations, individual values with concentrations below the limit of quantification were converted to half of the limit of quantification. Thus, the sample pair SW 9/1 appears below the limit of quantification line in the diagram.

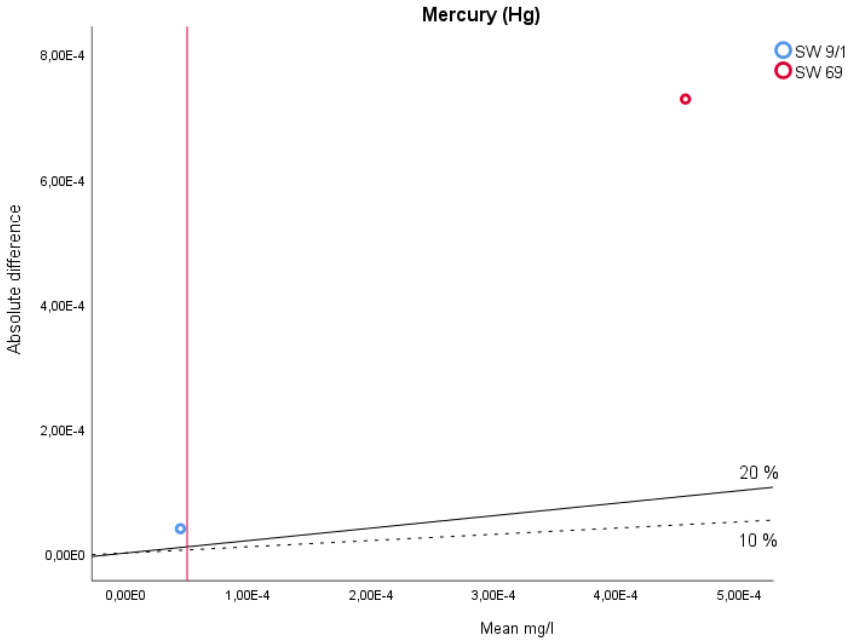

Figure 4.13. Thompson-Howarth-plot of Hg concentrations in surface water in the 1st sampling phase of the EnviTox-project. The mean of Hg concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for of Hg concentration (0.00005 mg/kg). In calculations, individual values with concentrations below the limit of quantification were converted to half of the limit of quantification. Thus, the sample pair SW 9/1 appears below the limit of quantification line in the diagram.

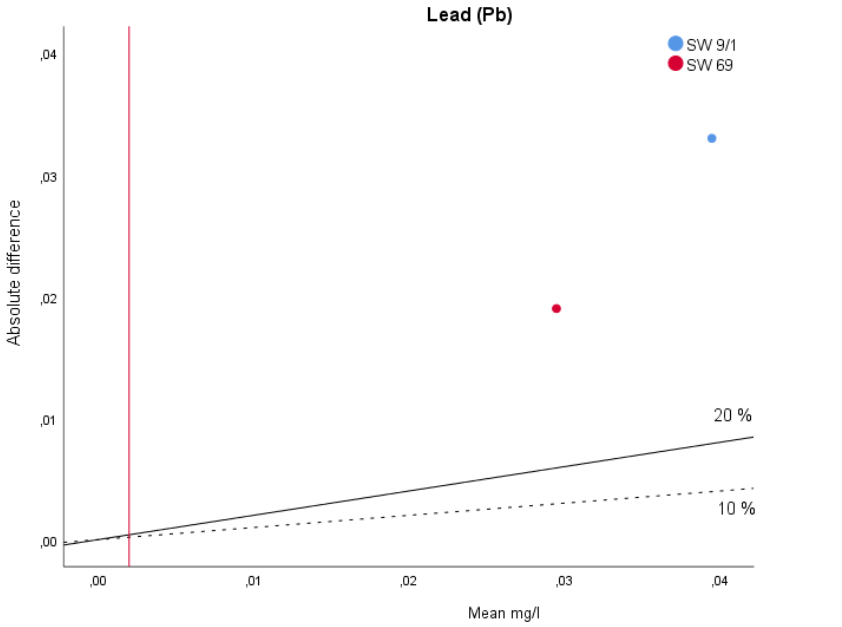

Figure 4.14. Thompson-Howarth-plot of Pb concentrations in surface water in the 1st sampling phase of the EnviTox-project. The mean of Pb concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for of Pb concentration (0.002 mg/kg).

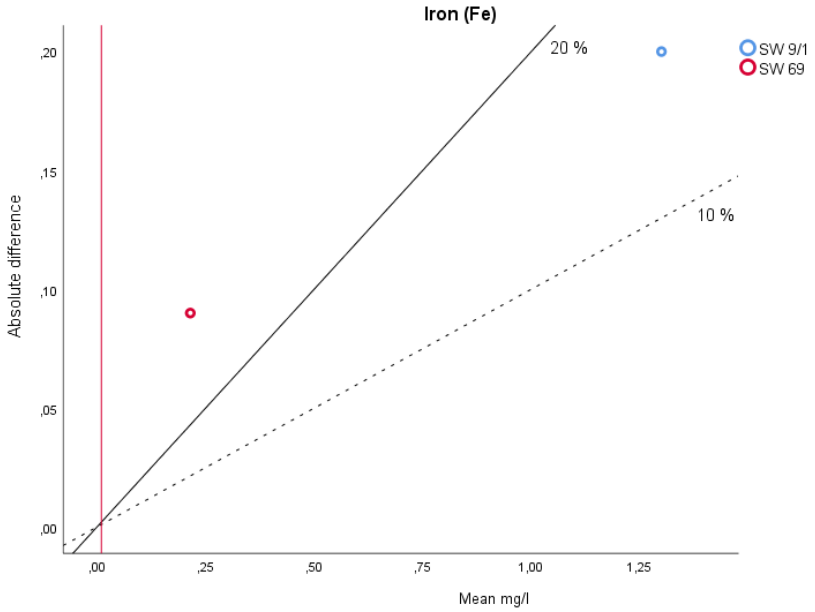

Figure 4.15. Thompson-Howarth-plot of Fe concentrations in surface water in the 1st sampling phase of the EnviTox-project. The mean of Fe concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for of Fe concentration (0.01 mg/kg).

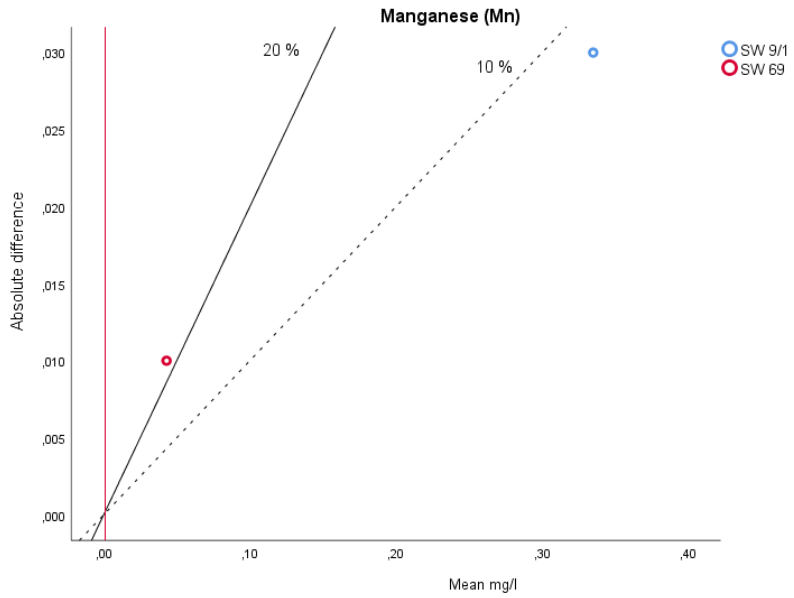

Figure 4.16. Thompson-Howarth-plot of Mn concentrations in surface water in the 1st sampling phase of the EnviTox-project. The mean of Mn concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for of Mn concentration (0.001 mg/kg).

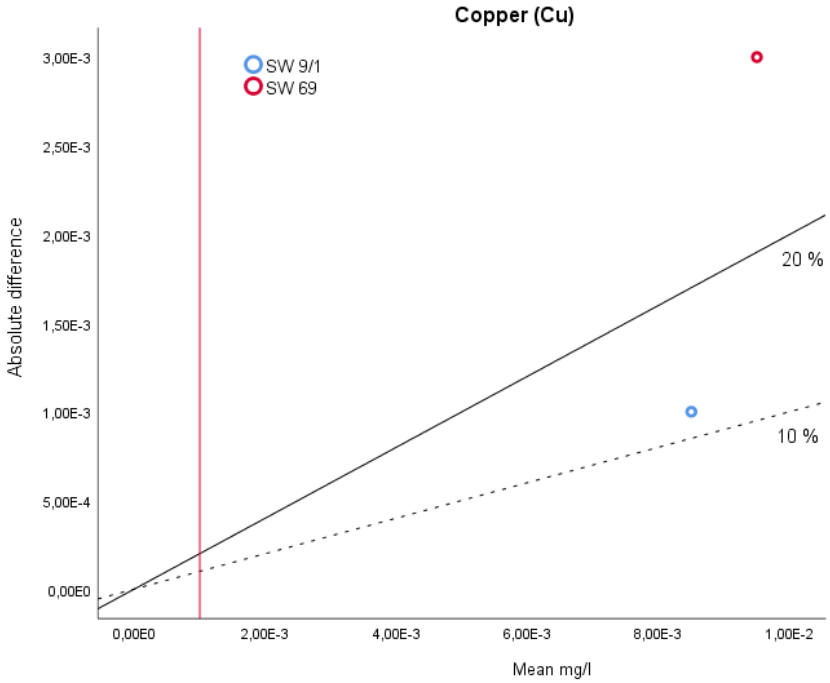

Figure 4.17. Thompson-Howarth-plot of Cu concentrations in surface water in the 1st sampling phase of the EnviTox-project. The mean of Cu concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for of Cu concentration (0.001 mg/kg).

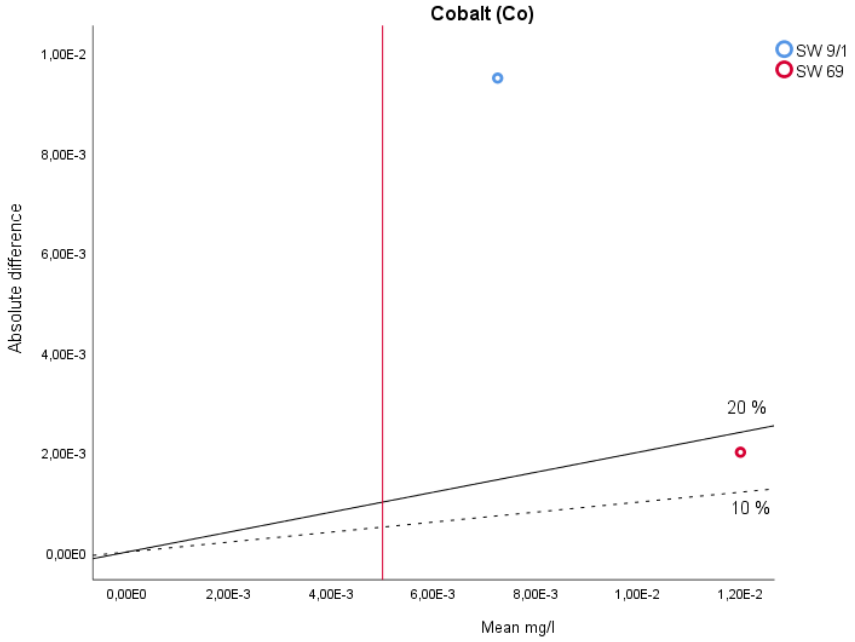

Figure 4.18. Thompson-Howarth-plot of Co concentrations in surface water in the 1st sampling phase of the EnviTox-project. The mean of Co concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for of Co concentration (0.005 mg/kg).

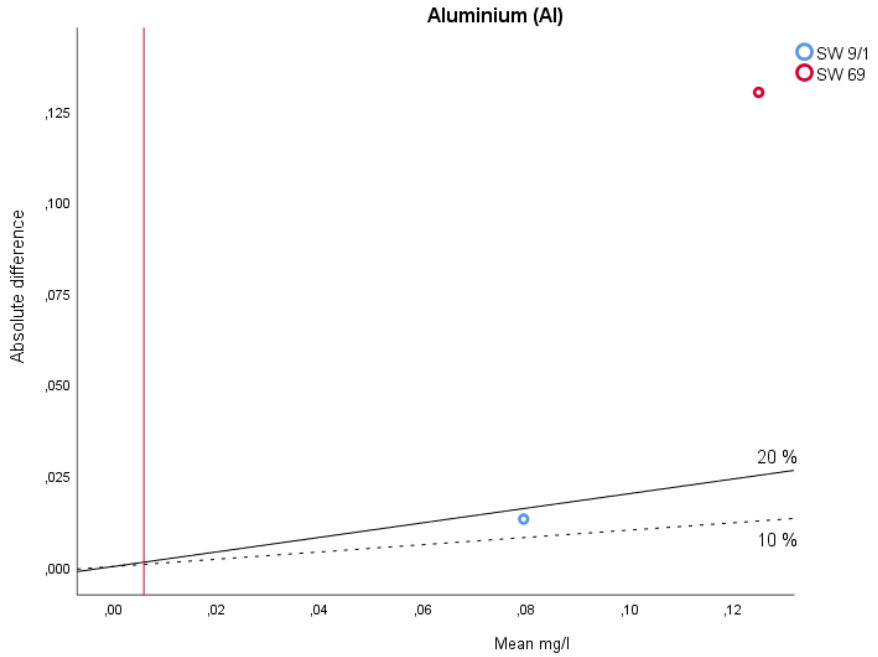

Figure 4.19. Thompson-Howarth-plot of Al concentrations in surface water in the 1st sampling phase of the EnviTox-project. The mean of Al concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for of Al concentration (0.001 mg/kg).

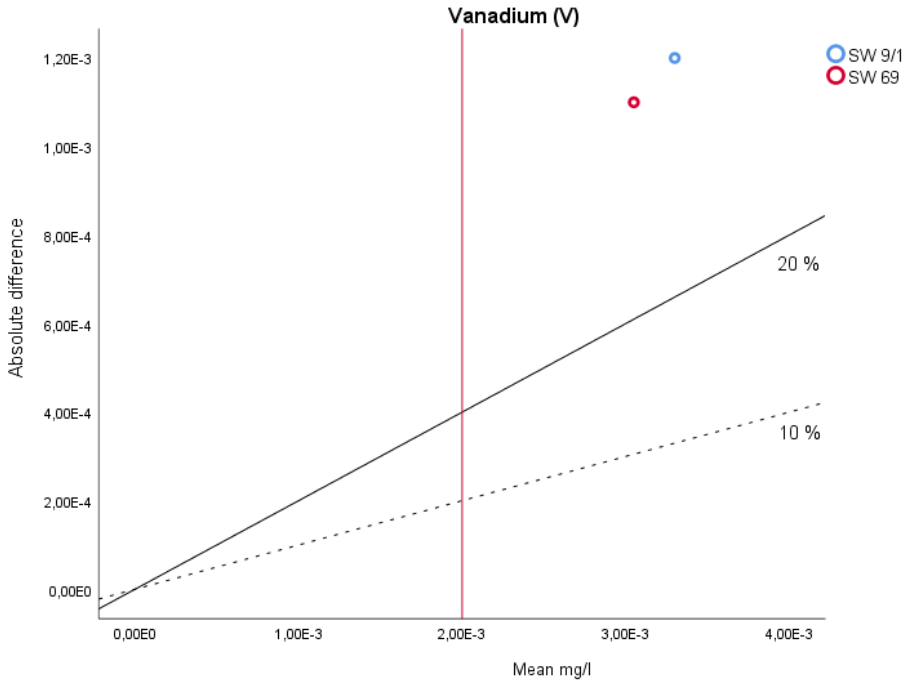

Figure 4.20. Thompson-Howarth-plot of V concentrations in surface water in the 1st sampling phase of the EnviTox-project. The mean of V concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for of V concentration (0.002 mg/kg).

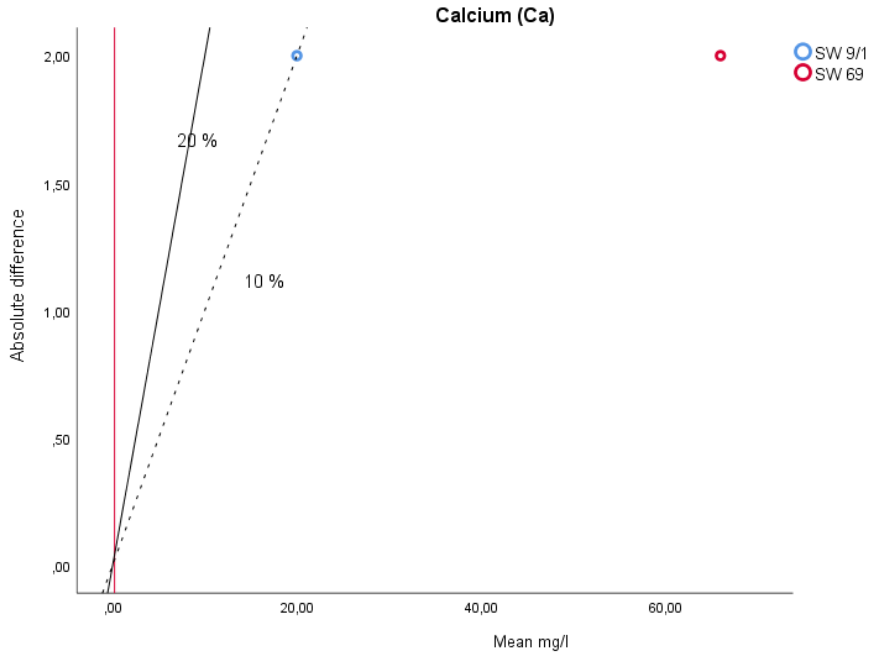

Figure 4.21. Thompson-Howarth-plot of Ca concentrations in surface water in the 1st sampling phase of the EnviTox-project. The mean of Ca concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for of Ca concentration (0.2 mg/kg).

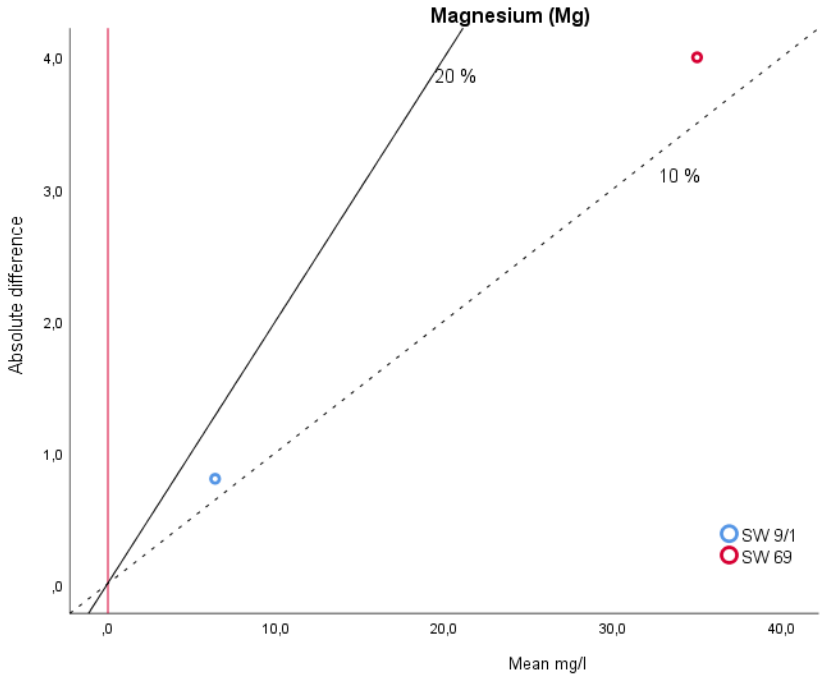

Figure 4.22. Thompson-Howarth-plot of Mg concentrations in surface water in the 1st sampling phase of the EnviTox-project. The mean of Mg concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for of Mg concentration (0.04 mg/kg).

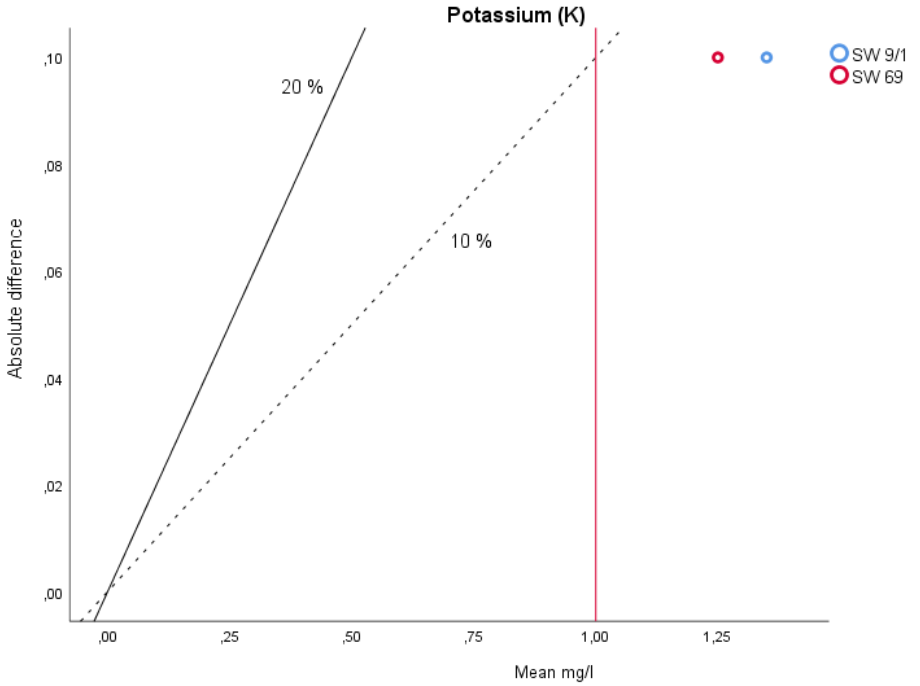

Figure 4.23. Thompson-Howarth-plot of K concentrations in surface water in the 1st sampling phase of the EnviTox-project. The mean of K concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for of K concentration (1.0 mg/kg).

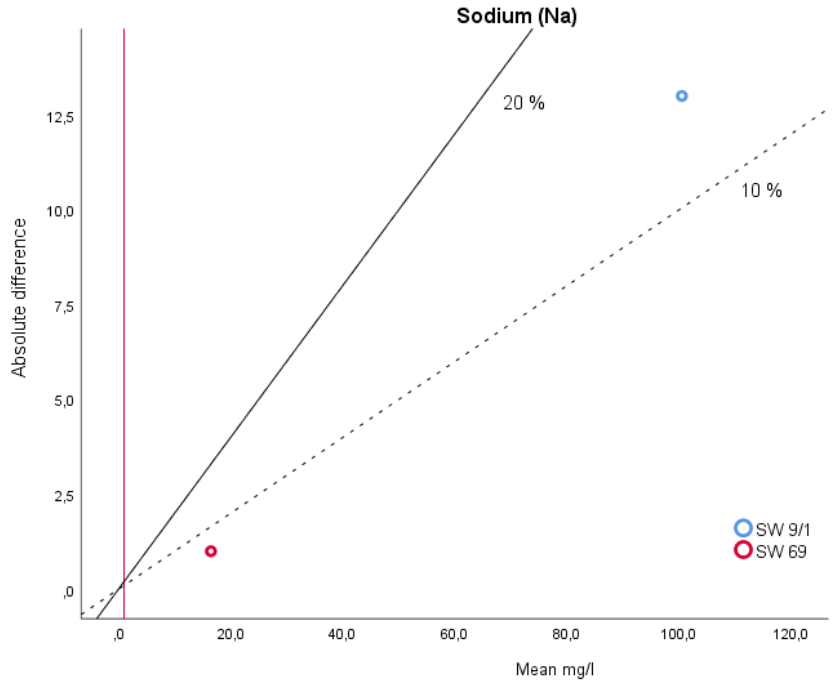

Figure 4.24. Thompson-Howarth-plot of V concentrations in surface water in the 1st sampling phase of the EnviTox-project. The mean of V concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for of V concentration (0.002 mg/kg).

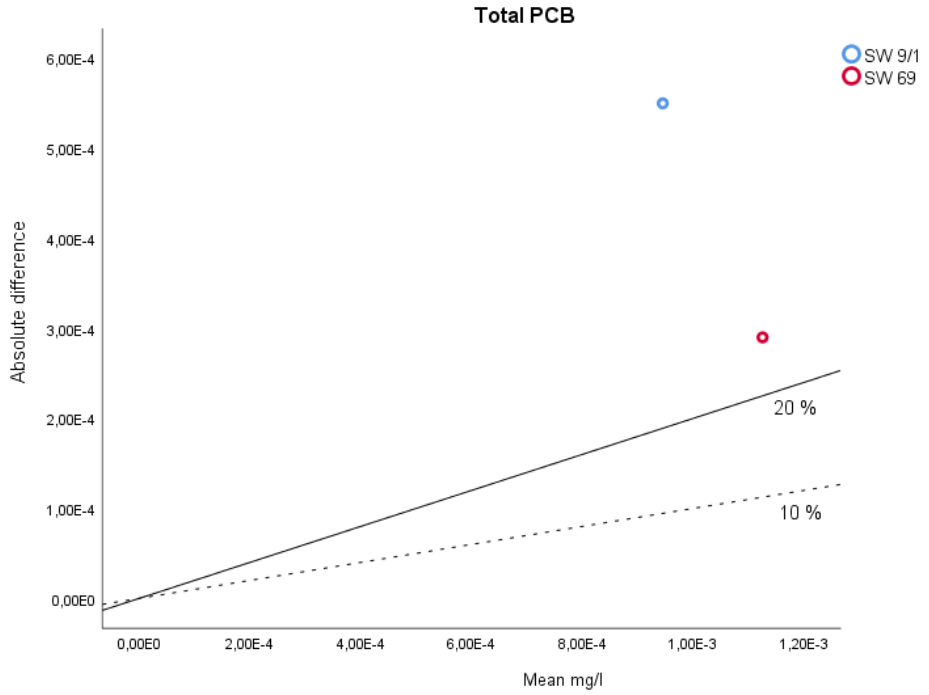

Figure 4.25. Thompson-Howarth-plot of total PCB concentrations in surface water in the 1st sampling phase of the EnviTox-project. The mean of total PCB concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis.

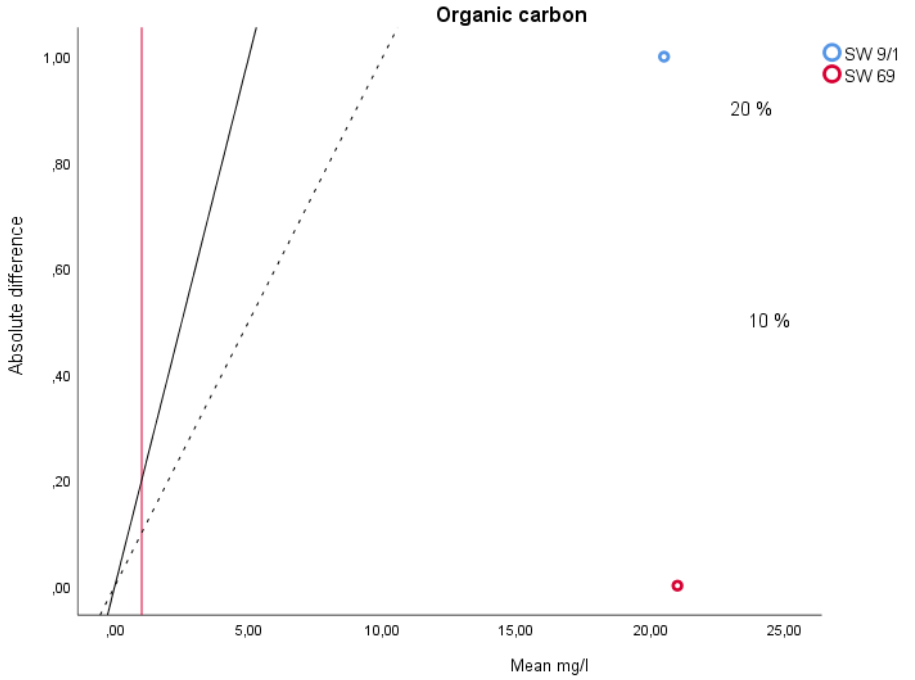

Figure 4.26. Thompson-Howarth-plot of organic carbon concentrations in surface water in the 1st sampling phase of the EnviTox-project. The mean of organic carbon concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for of organic carbon concentration (1.0 mg/kg).

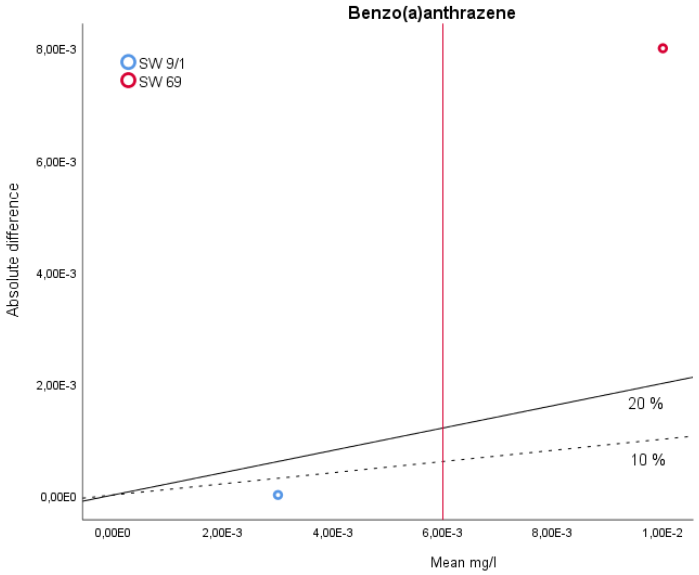

Figure 4.27. Thompson-Howarth-plot of benzo(a)anthrazene concentrations in surface water in the 1st sampling phase of the EnviTox-project. The mean of benzo(a)anthrazene concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for of benzo(a)anthrazene concentration (0.006 mg/kg). In calculations, individual values with concentrations below the limit of quantification were converted to half of the limit of quantification. Thus, the sample pair SW 9/1 appears below the limit of quantification line in the diagram.

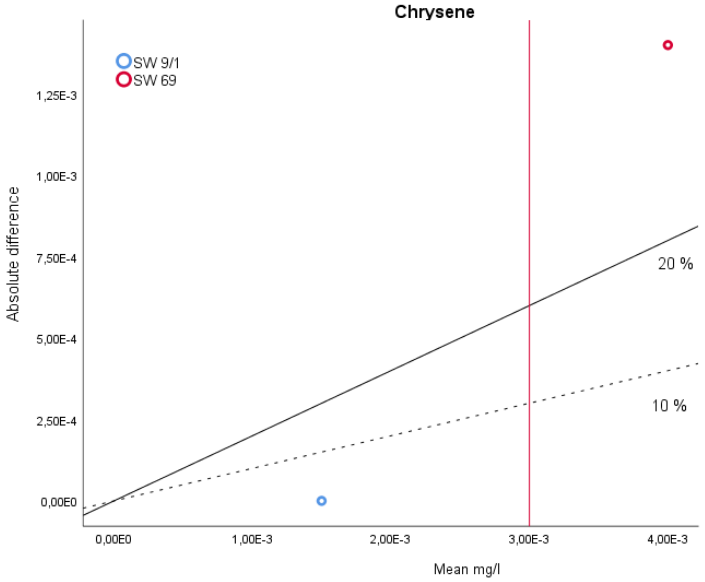

Figure 4.28. Thompson-Howarth-plot of chrysene concentrations in surface water in the 1st sampling phase of the EnviTox-project. The mean of chrysene concentration of the routine and field duplicate sample pairs is shown in the x-axis and the absolute difference between the samples in a pair is shown in the y-axis. The red line = limit of quantification for of chrysene concentration (0.003 mg/kg). In calculations, individual values with concentrations below the limit of quantification were converted to half of the limit of quantification. Thus, the sample pair SW 9/1 appears below the limit of quantification line in the diagram.