

ASROCKS-project (Guidelines for sustainable exploitation of
aggregate resources in areas with elevated arsenic concentrations)
LIFE10 ENV/FI/000062 ASROCKS

Downloaded from http://projects.gtk.fi/ASROCKS_ENG

ASROCKS-project is partly funded by EU's Life+ Environment Policy and Governance –programme.
Partners of the project: Geological Survey of Finland, Tampere University of Technology and Finnish
Environment Institute.

Sampling and Analysis

- Guidelines for aggregate production and construction sites in areas with elevated arsenic concentrations

Tarja Hatakka¹, Birgitta Backman¹, Timo Tarvainen¹, Paavo Härmä¹, Terhi Ketola², Pirjo Kuula² and
Jussi Reinikainen³

¹Geological Survey of Finland (GTK)

P.O.Box 96, FI-02151 ESPOO, Finland

²Tampere University of Technology

Korkeakoulunkatu 5, FI-33720 TAMPERE, Finland

³Finnish Environment Institute (SYKE)

P.O.Box 140, FI-00251 HELSINKI, Finland



Sampling and Analysis - Guidelines for aggregate production and construction sites in areas with elevated arsenic concentrations

Tarja Hatakka¹, Birgitta Backman¹, Timo Tarvainen¹, Paavo Härmä¹, Terhi Ketola², Pirjo Kuula² and Jussi Reinikainen³

¹Geological Survey of Finland

²Tampere University of Technology

³Finnish Environment Institute

1. Introduction

The main task in taking geochemical samples for the analysis of arsenic and other harmful elements is to have a sample which represents the study area and the study matrix as well as possible. The significant portion of the total uncertainty in site specific studies often comes from sampling. The reliable and representative sampling is based on a good sampling plan. It is recommended that the sampling personnel is accomplished and experienced in geochemical 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. Also the quality assurance and the safety matters should be taken into account.

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

The study areas vary considerably and each study area has its own properties, thus it is impossible to give the exact sample media as well as the exact number of samples that should be taken. They should be decided by each case.

2. Sampling plan

The main purpose of a sampling plan is to ensure the representativeness of the sampling. A representative sample means that based on it reliable estimations and evaluation about the properties of the environmental section where the sample has been taken could be done. The instructions for formulating a sampling plan could be found among others in standard EN 14899 as well as in many publications (for example in www.epa.gov/quality1/qs-docs/g4hw-final.pdf).

A sampling plan should include among others:

- The aim of the sampling and the sampling area
- Sampling sites and sampling dates
- Sampling manners and sampling methods
- Handling, transportation and storage of the samples
- Research and analysis methods
- Handling of the results and the reportage
- Quality assurance

3. Sampling in the ASROCKS project

The sample media used in the very first phase of ASROCKS project were bedrock, soil, products, surface water and groundwater. In the second phase also humus, stream sediment, pore water and dust samples were taken. From some of the rock and soil samples mineralogical analysis were carried out. The sample media used for the determination of arsenic concentrations depends on the local and regional environmental properties. The sample media which is suitable in Finnish environmental conditions may not be relevant to the other countries and vice versa.

3.1. First phase

In the first phase, the aim of the study is to find out if there are harmful arsenic concentrations in bedrock or soil. While a producer is planning to start a rock aggregate production, the arsenic concentrations in bedrock or soil in the production area could be analyzed from the samples that the producer anyway takes, for example the samples taken to find out the strength properties of the rock. From each main bedrock type 3 – 5 subsamples could be combined together as a composite sample. Also the arsenic concentrations in surface water and groundwater could reflect the arsenic concentrations in bedrock and soil.

Rock sampling

These guidelines for rock sampling are suited for the regions (provinces) with elevated arsenic concentrations in bedrock. Most of the enrichment of As in bedrock is directly related to natural processes, such as the activity of hydrothermal fluids. In such cases, extensive zones of low-degree As enrichment may be formed. Arsenic content varies widely in the rocks types of different kind. Arsenic-rich sulphides may occur in shear and contact zones of the bedrock and in some rock types evenly disseminated. Arsenopyrite is the most common As mineral in Finland, other minerals are among the others löllingite, gersdorffite and cobaltite.

It is suggested to carry out detailed geological mapping before making the sampling plan for rock samples. Rock samples must be taken from all the rock types in the target area which are planned to exploit as an aggregate product or construction area. Arsenic concentrations can be measured from the same rock samples that are used for determination of technical properties, or arsenic determinations can be made from composite rock samples made up from 3 -5 subsamples.

ASROCKS experiences:

In the ASROCKS project the rock samples of different kind were taken from bedrock, as follows:

- Pieces of rock or blocks of rock sample from bedrock
- Rock powder samples as a product of pressure air bore drilling equipments
- Rock powder samples directly from surface of outcrop drilled by a hammer drill
- Wet slurry samples taken from drill holes
-

On the basis of experiences in the ASROCKS project it is able to be noticed, that:

- From the homogeneous rock type both rock powder and rock piece samples gave analytical results of same level

- Differences in analysis between rock piece samples and rock powder samples were bigger when the rock type was heterogeneous and contains special characteristics (shear zones, dikes, enclaves, inclusions, fractures). Constant results were achieved from rock powder samples.
- There is contamination risk in wet slurry samples from drill holes

Also portable XRF equipment was tested in analyzing the rock samples. Measurements were carried out directly from surface of outcrop and rock powder drilled by hammer drill. Measurements by portable XRF from rock powder were more comparable to the laboratory analyses than measurements directly from the surface of outcrop. Variations in measurements taken directly from the surface of outcrops were bigger when the grain size of rock type grew up.

On the basis the experiences from the ASROCKS project and from the target area of the project, the investigation of arsenic concentration level in the bedrock requires one composite sample (consisting 3-5 subsamples) of every main rock type which occur in the target area and planned to rock aggregate production.



Fig. 1. Rock sampling using a hammer drill. Photo: Timo Tarvainen, GTK

Soil / Sand and gravel

The determination of arsenic concentrations is usually needed when sand and gravel production or construction is planned for a study area. Arsenic concentrations could be analyzed from topsoil and subsoil samples. In Finland the soil layers usually forms podzol soil, where the upper layer consists of organic litter and humus. Below the humus layer locates a leached horizon and below it an enrichment horizon. The lowest soil layer is unaltered soil, which in Finnish soils locates usually from the 75 cm depth to the bedrock surface. In Finland, the bedrock is largely covered with quaternary deposits. The most common soil type is till. The highest arsenic concentrations in till have been measured from the samples taken close to the bedrock.

The knowledge of arsenic concentrations in topsoil is needed especially when the study area is planned for settlement. The topsoil samples are taken from the minerogenic soil below the humus layer. The sampling depth in Finnish soils is usually 0 – 25 cm. The subsoil samples are taken from the unaltered soil. Usually, the subsoil samples in construction areas are taken at the depth of the planned digging depth while building. If the study area is planned for sand and gravel production, or if in connected with the construction, large earth moving operations will be done there, the subsoil samples could be taken from the altered soil at any depth despite the thickness of the quaternary deposits. In till areas the subsoil samples should be taken close to the bedrock surface where the arsenic concentrations are usually the highest.

The sampling method for taking geochemical soil samples depends on the aim of the study. The samples are usually taken as single samples when we try to find out if there are harmful amounts of arsenic in the soil of the planned production or construction area. If we try to find out the average arsenic concentrations in soils for example in the sand and gravel production area, the samples could be taken as composite samples.

Detailed sampling instructions could be found for example in the field manual for the geochemical mapping over Europe (Salminen et al. 1998, http://tupa.gtk.fi/julkaisu/opas/op_047.pdf).



Fig. 2. Soil sampling site.

ASROCKS experiences:

In ASROCKS project also some soil samples were taken from the fine-grained sediment of dried puddles in some production areas. Often, the arsenic concentrations were much higher in these sediments than in those of soil or bedrock, so in these production areas there is arsenic in air and ground as dust.

The arsenic concentrations in soils could also be determined with a portable XRF. Usually the arsenic concentrations measured with portable XRF were lower than the arsenic concentrations analyzed in laboratory. So, the arsenic concentrations measured with portable XRF should always be confirmed with laboratory analysis.

Surface water and groundwater

Water is the main conduit for arsenic in nature. The arsenic concentrations in water could tell if there is arsenic in soil or bedrock in the study area. However, arsenic can be in soil or in bedrock in a weakly dissolved form when also the arsenic concentrations in water may be low. Thus, water analysis is not merely enough, but also arsenic determinations from bedrock and soil are needed. The environmental impacts of a construction and a rock aggregate production are often monitored by the water analysis of the surface and groundwater from the study area and its surroundings. It is important to monitor the changes in the chemical composition or the properties of water as well as arsenic concentration because they tell about the environmental conditions where the water lies. The determination of the arsenic concentrations of water, especially of well water, is usually producer's as well as well owner's advantage. In addition, the water quality studied before the production starts, channels the allocation of the water system control during the production. Also in the catchment areas, where the planned production site locates, a hydrological mapping, which includes the estimation of the current directions of surface water and groundwater as well as the run-offs, should be carried out.

The surface water samples could be taken from ditches, streams, rivers, ponds or lakes in the planned production or construction area or widely from the whole catchment area. Groundwater samples could be taken from springs, dug wells, drilled bedrock wells, drill holes and groundwater observation tubes locating in the catchment area. If there are no suitable sampling points for groundwater in the catchment area, the arsenic concentrations in groundwater from a drilled bedrock well further, but in like bedrock type, could give some reference about the occurrence of arsenic also in the bedrock of the study area. Groundwater reflects very well what compounds and elements are dissolving in it from bedrock and soil, in the prevailing environmental conditions.

Water samples for the arsenic analysis can be taken also from pore water which is moving in soil or in product piles. These results could be used for estimation of how easily arsenic dissolves from the rock material.

Total arsenic concentrations in water are analyzed from an unfiltered sample and dissolved arsenic concentrations from filtered samples. The laboratory where the arsenic concentrations could be analyzed gives more detailed instructions for water sampling, and they can give relevant equipment for it too. Detailed geochemical water sampling instructions could be found also for example in the field manual for the geochemical mapping over Europe (Salminen et al. 1998, http://tupa.gtk.fi/julkaisu/opas/op_047.pdf).

ASROCKS experience:

While water samples are taken from observation tubes or drill holes it is important to pump the water enough before the sampling, and preferably take the samples from pumped water than with a bailer whenever it is possible. According to the results received in ASROCKS project the arsenic

concentrations in groundwater in a drill hole differ notably from each other depending on the sampling method. The sampling method affects to the amounts of dissolved and total arsenic too.



Fig. 3. Soil water sampling from an aggregate pile using a lysimeter. Photo: Timo Tarvainen, GTK

3.2. Additional sampling materials for detailed studies

Stream sediment

The element concentrations of stream sediments reflect the chemical composition of soil and bedrock in the catchment area and the local environmental conditions. The stream sediments represent long-term environmental load. The arsenic concentrations of stream sediments could be used for the estimation of arsenic concentrations in bedrock and soil, and in addition, during the aggregate production the monitoring of arsenic concentrations in stream sediments helps to evaluate the effect of the production on the arsenic drift from the production area to the environment, and to how far the arsenic is carried.

Detailed geochemical stream sampling instructions could be found for example in the field manual for the geochemical mapping over Europe (Salminen et al. 1998, http://tupa.gtk.fi/julkaisu/opas/op_047.pdf).



Fig. 4. Brown arsenic containing Fe-precipitates sediment near an aggregate production site. Photo: Arto Pullinen, GTK.

Dust

Dust particles are one potential pathway of arsenic from the aggregation production site to the surroundings. Air quality target value for arsenic is 6 ng/m^3 (annual mean value) measured on the PM_{10} particle size fraction. While planning a new aggregate production site the arsenic concentrations in dust can be roughly estimated based on As concentrations in rock. However, during operation a long term dust (PM_{10} particle size fraction) sampling and analysis is used to measure the actual concentrations. Sampling can be carried out according to reference method EN 12341:1999 (Determination of the PM_{10} fraction of suspended particulate matter). Situation of blasting, crushing and other operations in the production site as well as wind directions should be taken into account in the sampling plan.

ASROCKS experience:

In ASROCKS project, arsenic concentrations in dust particle were measured from the Nokia demonstration site by the Finnish Meteorological Institute (<http://en.ilmatieteenlaitos.fi/air-quality-services>). Two short sampling periods were selected for demonstration purposes: July 2013 during the time of aggregate material transportation in dry summer conditions and March 2014 during crushing and sieving on the site. Sampling followed the reference method EN 12341:1999 and analyses were based on standard method EN 14902:2006. Arsenic concentrations were much lower than the annual mean target value of 6 ng/m^3 . The selected sampling and analytical methods were suitable for aggregate production site but longer sampling time would have been needed for reliable comparison with annual mean target value.

Humus and other organic samples

Humus is the topsoil horizon, it is organic matter which contains decomposed remains of plants and animals and their waste products. Also airborne material is gathered into humus. The arsenic concentrations in the humus show has the arsenic rich dust spread in the environment. The arsenic concentrations and the changes in those help to evaluate if the arsenic rich dust from the production area is spreading in the surroundings, and how far it is spreading.

Detailed geochemical humus sampling instructions could be found for example in the field manual for the geochemical mapping over Europe (Salminen et al. 1998, http://tupa.gtk.fi/julkaisu/opas/op_047.pdf).



Fig. 5. Humus sampling. Photo: Arto Pullinen GTK

Berries and mushrooms

The arsenic concentrations in berries and mushrooms close to production area are usually determined if it is assumed that people are picking and eating them from the surroundings. The main purpose is to ensure that the arsenic concentrations in berries and mushrooms are not the high causing any risk to human health. The laboratories analyzing arsenic concentrations in food give the detailed instructions for berry and mushroom sampling.

4. Quality assurance

The quality assurance contains of all the operations which are used to ensure that the received results fit the made demands. The uncertainty of the sampling is identified, measured and controlled with quality assurance samples (among others Westerholm 2010).

To ensure a good quality geochemical sampling the personnel of the sampling should have relevant certificates for sampling (in Finland http://www.syke.fi/fi-FI/Palvelut_aineistot/Ymparistonaytteenottajien_henkilosertifiointipalvelu) and previous experience in geochemical sampling.

For different soil, rock, product, humus, sediment and leaching test samples should be taken duplicate samples at least 5 % of the total number of the samples for to ensure the quality of sampling. The

duplicate samples are taken the same way as the normal samples (Salminen et al. 1998, http://tupa.gtk.fi/julkaisu/opas/op_047.pdf).

The quality of water samples is ensured with blind samples (0-samples). The blind samples are prepared from deionized water the same way as the normal samples. At least 5 % of the total number of the water samples should be quality assurance samples.

Accredited testing laboratories enforce their own customary quality assurance methods.

5. Laboratory analysis

The geochemical samples are taken to an accredited laboratory for analysis. While choosing the laboratory the detection limit for arsenic should be taken into account and ensure that the detection limit for arsenic in the analyze method of the laboratory is lower than 5 mg/kg. The 5 mg/kg is in Finland the threshold value for arsenic in the Decree on the Assessment of Soil Contamination and Remediation needs (214/2007).

Rock, product and soil samples are sent to an accredited laboratory which analyzes them according to accredited methods. Solid rock and product samples are crushed (> 70 % <2 mm) and the *aqua regia* leachable concentrations of arsenic are determined. The rock powder and the pulverized rock samples are sieved to < 2 mm grain size if needed, and the arsenic concentrations are analyzed the same way as the other rock samples. The soil samples are dried and sieved to the grain size < 2 mm in a laboratory. The *aqua regia* leachable arsenic concentrations are determined using the accredited methods.

The leachability of arsenic in rock, soil and product samples could be examined with weak leaches for example ammonium acetate-EDTA leach and with leaching tests.

From water samples, the arsenic concentrations are determined using ICP-MS technique.

6. Monitoring

Aggregate products

The production samples of rock aggregates, sand and gravel and till are usually taken when the production has already started. The samples for geochemical determinations could be taken from the product piles as well as from the belt conveyor during the production. The arsenic concentrations could be analyzed from single samples or from composite samples, this depends on the aim of the study. The composite samples represent better the average composition of a pile while the adequate amount of single samples shows better the total deviation of the composition. The results of arsenic concentrations in product piles are used for the risk management purposes during the operation and for the estimation of the quality of the product at the usability point of view.



Fig. 6. Aggregate sampling for a leaching test.

ASROCKS experience:

In the first phase, the product samples for laboratory analyses were taken around the product pile. Six samples with the highest arsenic concentrations were measured with portable XRF. In the second phase, three different sampling methods were tested:

The leaching test method was based on SFS-EN 932-1 standard. A loading shovel made a stack of the product pile's material, and a composite sample was taken from it. For these samples, one duplicate sample was taken. The multi-increment sampling method was based on increment subsampling (Gerlach & Nocerino 2003) but the original sampling method was adapted to the ASROCKS project. 30 to 50 subsamples were collected around the product pile and they were combined as a composite sample. For these samples, two duplicate samples were taken. In the third method, six subsamples were taken around the product pile and the samples were combined together as a composite sample. One duplicate sample was taken in this method. All the samples were dried and crushed in the laboratory, and the arsenic concentrations were determined with XRF and from *aqua regia* and ammonium acetate-EDTA leach. The arsenic concentrations were also measured with portable XRF before they were sent to the laboratory. The results show that in the cut products (grain size from at least 2 mm) the variation in arsenic concentrations is lesser than in the products which contain the finest fractions (Fig. 7). Also in cut samples, the sampling method does not play a very important role (Fig. 8). The variation of arsenic concentrations is lesser in the samples taken with the multi-increment sampling method, and these samples present the best average arsenic concentrations in the product piles (Fig. 8). However, the adequate amount of single samples shows better the total deviation of the composition, thus the minimum and maximum values could be found (Fig. 8).

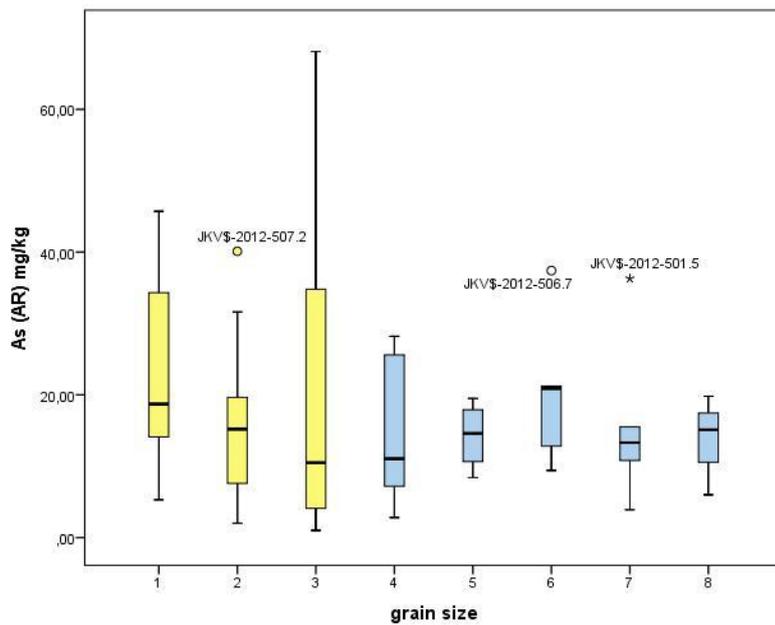


Figure 7. The arsenic concentrations (*aqua regia* leach) in rock aggregate products classified by the fraction sizes of the product. Products' fraction size 1= 0-2 mm – 0-4mm (n = 10), 2 = 0-6 mm – 0-16 mm (n = 24), 3 = 0-31 mm – 0-400 mm (n = 13), 4 = 2-6 mm – 2-56 mm (n = 6), 5 = 3-6 mm – 4-18 mm (n = 4), 6 = 5-11 mm – 6-11 mm (n = 5), 7 = 8-16 mm – 11-22 mm (n = 6) and 8 = 16-32 mm – 30-50 mm (n = 3).

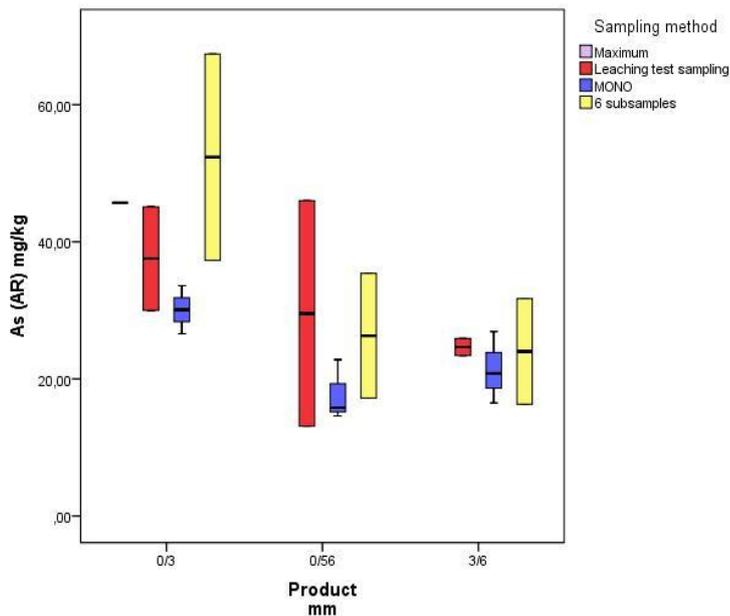


Figure 8. Arsenic concentrations (*aqua regia* leach) in product samples classified by the grain size of the product and by sampling method. Grain size 0/3 = 0 – 3 mm, 0/56 = 0 – 56 mm and 3/6 = 3 – 6 mm. Leaching test sampling = leaching test sampling method, MONO = multi incremental sampling method and 6 subsamples = six subsamples method.

Surface water and groundwater

Water is the main conduit for arsenic in nature. The environmental impacts of a construction and a rock aggregate production are often monitored by the water analysis of the surface and groundwater from the study area and its surroundings. It is important to monitor the changes in the chemical composition or the properties of water as well as arsenic concentration because they tell about the environmental conditions where the water lies. In Finland, the seasonal variation affects on the amount and the quality of surface water and groundwater. This must be taken into account while planning the water monitoring in production areas and in their surroundings.

Additional monitoring sample media

In addition to aggregate and water samples, As concentration in dust and sediments can be monitored around the productions sites. Dust sampling has been discussed earlier in the sampling chapter. Stream sediments and lake sediment profiles can be used to estimate the long term accumulation of arsenic in the environment. This kind of monitoring was not tested during the three year ASROCKS project.



Fig. 9. Stream sediment sampling. Photo: Arto Pullinen GTK.