

Mobile dust sampling device for dust filter generation at a Ni refinery

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To study the distribution of Ni emission to air from the myriad of point and diffuse sources within a plant site is a complex sampling and analysis problem. However, it provides important underlying information for source abatement. At a Ni refinery in Southern Norway such sampling of Ni in air in close proximity to sources with subsequent analysis of content or particle structures by various methods has always been a complicated endeavour with no or inconclusive results. The main difficulty lies in obtaining both a representative and a large enough sample size to achieve quality results within a reasonable cost budget.

Normally a filter sample of dust used for the chemical analysis of Ni in air is collected with fairly expensive reference instrumentation. If more than one filter sample is needed, e.g. several copies of a specific sampling period and location, several co-located instruments should be used, or one filter is cut into several pieces for post-analysis. Cutting a filter in pieces will compromise the sample and chemical analysis and most reference PM samplers are not easily or cheaply operated and transportable.

Thus, a novel in-house sampling device that delivers 3 independent and parallel filters simultaneously was constructed. The goal was to obtain triplet sample sets from many locations inside the plant area. The sample sets could be screened for Ni levels and provide filter copies for advanced chemical analysis when needed. Comparisons of individual samples in sets of varying Ni content showed satisfactory equivalence.

The sampling device is continuously used in a pilot Ni ambient distribution study within the plant site. The triplet sampler has been rotated at more than 10 sites since 2015. The sites varied between being on the ground and on roof tops of buildings. Some locations were near potential sources that give diffuse emissions of nickel dust. Results have been used to understand the Ni variation spatially and to identify important contributing sources to the total Ni emissions that potentially is emitted to the surrounding airshed. Parallel samples have been sent for more advanced post-analysis for periods with known elevated nickel concentration. The results have yielded more defensible abatement plans and more effective abatement measures.

Introduction

Glencore Nikkelverk AS was founded in 1910 and is one of the world's largest nickel refineries with a production capacity of 92 000 tons of nickel. The refinery also produces cobalt, copper, and sulphuric acid. The products from the plant are high purity and used in electronics, jet engines, electrical vehicles, medical equipment's etc. The nickel plant is situated within the city limits of Kristiansand (Norway) about ~1.7 km in distance to the city centre. Kristiansand is Norway's fifth largest town, with a population of ca 110 000 people.

The process at the facility has been developed organically over more than 100 years, making for a very complex plant layout, with many buildings and internal intermediate transportation routes. Figure 1 shows the plant and points to 11 different process units. The raw material is mainly "matte" received in bulk from Glencore operations in Sudbury, Canada, by ships, as well as matte and other intermediates received in 1 ton bags from other suppliers. Matte is a polymetallic sulphide material where Ni, Co, Cu and Fe are the main metals. The raw materials are treated in several hydrometallurgical stages that involves leaching, filtrations, precipitation and electrowinning. Furthermore, they can undergo processing in fluidised bed rosters and melting furnaces. The Ni plant has annual emissions limits to air for Ni (0,75 tons) and for Cu (1,05 tons). The emission permit also regulates total dust, some other gaseous species and more specifications not relevant here. The operating permit covers all defined point sources and diffuse emissions. Diffuse emissions are all sources of dust that are not channelled and captured by a treatment process or come from more mechanical processes outdoors.

The Nikkelverk is the main source to ambient nickel concentrations in the Kristiansand area, which by standard methodology is defined as the Ni concentrations in PM₁₀ (Particulate matter with an aerodynamic diameter under 10 micrometres). In Norway the air quality norm for Ni concentration is 20 ng/m³ as an annual average. In 2009 the plant together with Kristiansand municipality started to measure ambient Ni, Cu and Co at one location (No 12 in Figure 1) near the fence line of the plant. The typical yearly average since then have been slightly above the national norm, and the factory has made large efforts and investments to decrease Ni emissions from the plant.

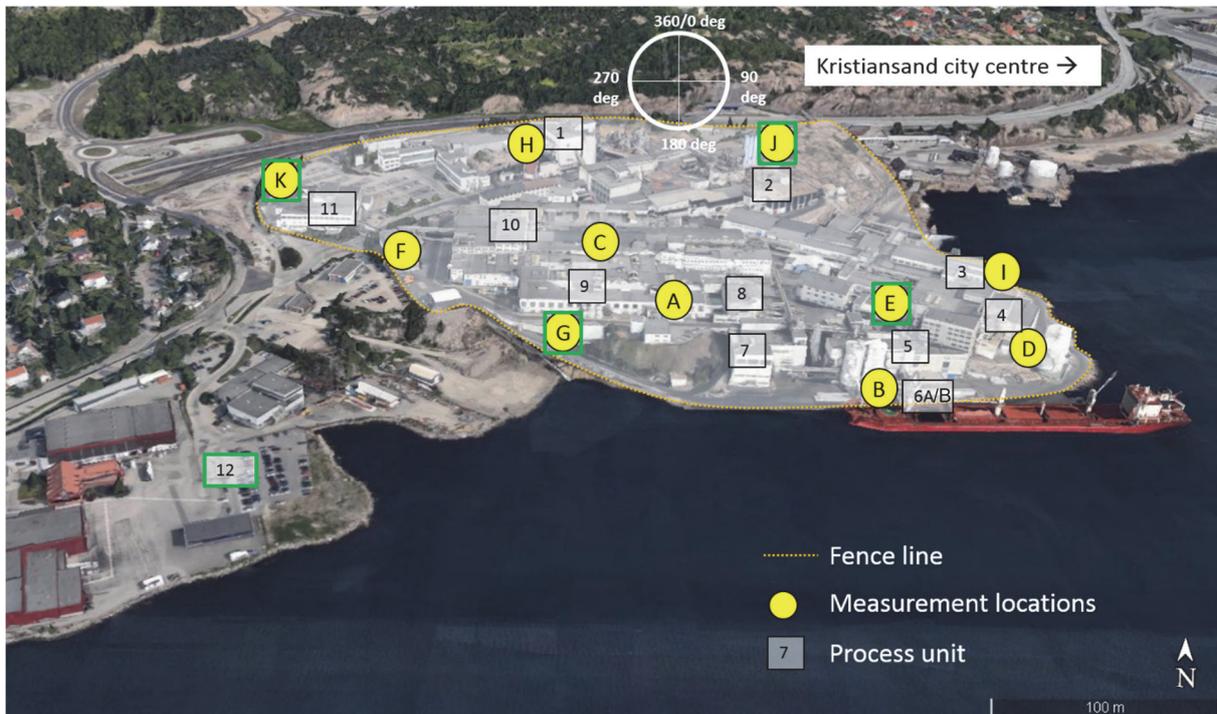


Figure 1. Aerial overview of the Nickel plant and the surrounding area. The numbers 1-12 refer to some of the different production process units, and the letters refer to sampling and measurement positions (A- K) that have been used within the plant fence lines. Position 12 is the reference measurement site in the national PM network. (The green squares indicate measurements sites that were used for another more in-depth PM study not included here.)

In order to prioritize further actions and investments an evaluation of the typical contribution of Ni emitted from each process area was needed. Modelling the contributions to the existing fence line monitoring location gave inconclusive and highly uncertain results. More advanced physicochemical analysis, e.g. ICP-MS, ED-XRF, SEM, Raman on randomly picked PM₁₀ filters from the fence line site also did not provide significant results. The purpose of these additional analyses has been to characterize the nickel compounds in more details, such as sulphates, sulphides, chlorides etc., because they can be linked to different process units. The main problem is sending a collected filter of dust with unknown Ni content to an expensive analysis that could potentially yield no usable results. Thus, often costly analytical work was done with limited practical results.

Multiple and fairly equivalent co-located filters sampled together were needed, to avoid the problem of sending dust filters with low amounts Ni containing dust to advanced physicochemical analysis. Furthermore, the ambient concentration of nickel at most positions within the plant will very much depend on local wind and weather conditions¹. The samples will thus vary in time based on just weather effects, and a large sampling number is consequently needed. The Ni refinery also needed a sampling device that was easy to place at different sites on the plant, and ground level, on top of the roofs etc. This would give the flexibility to get contribution data from different process units around the plant.

It was therefore decided to construct a new simpler sampling device that could yield more than one sample simultaneously. The idea was to build a sampler that could give order of magnitude data with satisfactory quality for continuous abatement work to reduce Ni emissions. It was also very important that additional chemical analysis could be done on samples taken at the same time and same place on filters we already knew had a significant level of nickel mass. The purpose was not to have a certified reference sampler for legal reporting or perform any absolute contribution calculation from any process unit. Total emission monitoring and reporting according to compliance with operating permits are done independently to this project. Calculating Ni emission factors from diffuse sources is more costly and resource intensive as it requires a much higher time resolution in Ni concentration measurements, meteorological data must be recorded, and reverse dispersion modelling must be used in addition to measurements². It will also require a more detailed approach with respect to TOS to adequately represent the emission sources as diffuse dust sources are very heterogeneous in nature, with regards to composition and concentration levels.

This paper will describe the initial work on making a novel multi-sampling device for PM₁₀ filters to gain spatially distributed filter sets for post-chemical analysis. We will show some initial data to verify the function of the sampler and disclose some of the pilot results. The sampling device has provided the plant with a smarter and cost-efficient methodology to detect, monitor and document ambient trace metal concentrations within fence lines.

Most ambient Ni concentration studies are done to document air quality outside plant fence lines, deposition to the biota, or inside buildings during occupational hazard studies³⁻⁸. Not many studies have been conducted to investigate the ambient Ni concentration distribution inside the plant lot. However, a similar study was done for another air pollutant class of compounds, PAHs, inside a steel plant⁹. Other methods of detecting Ni emission "leaks" do not exist, but camera detection can be used qualitatively today for dust and gases^{10, 11}.

Construction requirements and initial operation of new filter sampling unit

Design and construction of the new filter sampling device was focused on several important requirements as follows. The main requirement was that it could filtrate air onto three filters simultaneously that would be fairly identical to be used for parallel physicochemical analyses. The unit should be able to operate for at least 7 days without inspection. Further requirements were that the unit should be easy to transport by a forklift or that two persons could carry it. It should require very little maintenance, also be easy

to dismantle, trouble shoot and require no re-calibration upon doing so. Operators should be able to change filters and adjust device settings with minimal training. Weather shouldn't be a factor for operation, and thus the unit should be able to withstand weather conditions and temperatures in Norway. Several commercial filter types should be able to be used since chemical analysis requires different filter types. Last, the cost should be below approximately 15 000 €.



Figure 2. The sampling device is about 1 m long by 0.40 m tall. The unit can be moved easily with a forklift or manually.



Figure 3. Shows the inside of the box, with the air chamber, flow meter and pump. The wide diameter of the air chamber is large compared to tubes to each sampler, which gives fairly equal airflow through each filter. The flowmeter was calibrated before deployment of the unit.

Design and construction were done in-house at the Nikkelverk. The unit obtains three PM₁₀ filters simultaneously by subjecting Norwegian Institute of Air Research (NILU) standard PM₁₀ filter holders to a constant airflow of 10 lpm (Figure 2). A fourth filter holder was added but has no airflow and provides a blank filter collection set-up. The NILU filter holders consist of a filter holder and an attached PM₁₀ cut-off tube. These are an older type of standard NILU PM₁₀ filter holders that have been configured into the weather-proof box holding the air flow system and pump (Figure 3). The case was made by glass fibre material. The system is light, easily moved with a forklift or by people, and can be placed on the ground or on roofs around the plant site. The initial test runs showed that it could be operated within temperatures ranging from -15C to +25C. Sampling times have varied from 5 – 16 days without significant problems.

Method development and validation

The goal was to obtain triplet sample sets from many locations inside the plant area. The sample sets could be screened for elevated Ni levels and provide filter copies for advanced chemical analysis when needed. To achieve the Ni screening and to obtain data for investigating the spatial ambient Ni distribution, one has to continuously characterize one filter of each set as the device is moved around. To be able to do this routinely and with manageable cost the nickel plant's own in-house chemical analysis was chosen. The in-house chemical analysis of Ni on PM₁₀ filters is similar to the European standard NS-EN 14902:2005, where a filter is dissolved in acid, and ICP-MS is used for metals quantification of the solution. The sampling unit was tested with nitrate cellulose filters, pte- filters and quartz fibre filters. All the filter types were found to be usable, however the nitrate cellulose filters were selected for use in further pilot studies since they fit the best with the chemical analysis for metals done routinely at the nickel plant laboratory.

The total weight of PM₁₀ dust on the filters were not measured as this requires a very resource intensive set-up and is not really impacting the Ni evaluation study. The main reason for this is that Ni mass and PM₁₀ mass is not highly correlated. In measurements done at the fence (position 12 in Figure 1) Ni was only 0,2% of total PM (measured as 24h filters every 6th day over several years) and the linear correlation coefficient was 0,04. The average total PM₁₀ mass was 12,7 µg/m³ (Standard deviation: 20,2 µg/m³).

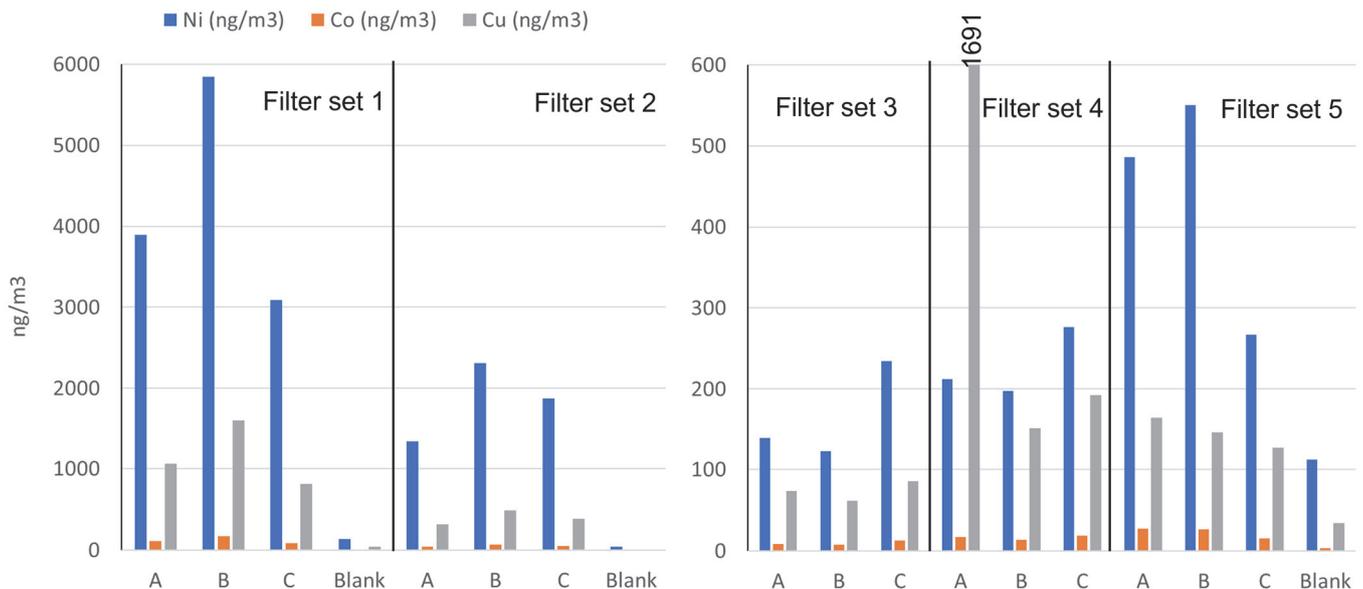


Figure 4. Overview of data from inter-comparison of Ni, Co and Cu concentrations from 3 filters in five sets of varying Ni mass. The blank is shown for 3 sets. Filter set 4 has one outlier.

Table 1. Comparison on two laboratories' analyses of two individual filters for Ni, Cu, Co, and Fe content per filter.

Metal in PM ₁₀	In-house (mg)	NILU (mg)	Difference (%)
Ni	0,13	0,125	104 %
Co	0,01	0,006	101 %
Cu	0,05	0,051	108 %
Fe	0,02	0,018	125 %

Table 2. results from chemical analysis of filter sample sets of varying Ni Content. Average metal concentration in air is showed with the calculated standard deviation also given in percent.

Sample period	n	Ave. Ni (ng/m ³)	Std dev. (%)	Ave. Co (ng/m ³)	Std dev. (%)	Ave. Cu (ng/m ³)	Std dev. (%)
14.-28. May 2020	2	165	61 (37%)	10	2,5 (26%)	74	12 (16%)
16.-24. April 2020	2	229	42 (18%)	16	2,6 (16%)	678	877 (129%)
8.-14. May 2020	3	435	148 (34 %)	23	6,8 (29%)	145	18 (13%)
17.-24. Oct. 2019	3	4276	1416 (33 %)	124	45 (37%)	1155	399 (35%)
1.-16. Aug. 2019	3	1838	486 (26%)	56	13 (22%)	397	85 (21%)

Two preliminary tests were done to qualify the sampling device and the in-house laboratory for routine Ni screening of each sample set. First, a comparison of two filters by was done. The in-house analysis was compared to a reference laboratory (NILU) for metals in PM₁₀. The two filters were from location G in 2016. Second, three filter sets with different Ni content analysed at the in-house laboratory were compared.

The comparative analysis of Ni, Cu, Co, and Fe content on two individual filters from one set analysed by two different laboratories. The agreement for the metals was within 4-21% and deemed good enough for using the in-house chemical analysis as the preferred routine Ni analysis. This is shown in Table 1. Five sets of 3 filters from 2019 and 2020 were used to check filter equivalence. The sets had varying Ni mass and were from a few different locations. Blank subtraction and hours of operations with a constant flow are used in calculating the air concentrations. A standard deviation between 18 to 40% was achieved for Ni concentration across the varying masses. Results for Cu and Co are consistent with Ni results. Table 2 and Figure 4 summarizes these data and results. In comparison, method precision calculated from co-located filter samplers that includes both sampling and chemical analysis error for Ni in the US IMPROVE network was 32% % for a study of PM_{2.5} filters¹². Blanks collected with every set in the new sampling device were examined often and showed results near zero for Ni, Cu and Co (Figure 4).

Results and discussion

An initial pilot study showed the usefulness of the novel sampling device. The average Ni concentration based on the Ni screening efforts was characterized for 10 measurement locations within the plant lot to evaluate the spatial Ni distribution. The unit was rotated at more than 10 sites within the plant area from 2016 until 2022. The sampling periods were in total 3-8 weeks at each location. Typically, filters were collected for one week at a time. The sites varied from being on the ground and on building rooftops. Some locations were near potential sources, while others were not. The average ambient Ni concentration at measurement locations A – K within the plant area is shown in Figure 5. Location 12 is approximately at sea level, while location J is at the highest point at the plant at about 30 m above sea level to give an idea of the landscape shown in Figure 1. All Ni values presented in the results have been blank corrected. [Figure 5 near here]

Results indicated that especially one region of the factory (sites A through-E) had significantly higher Ni concentrations showing than as measured outside the plant area at location 12. Special consideration is also put on site A in Figure 5, where measured Ni concentration is presented before and after a silo investment done in 2016-2017. The new silo made it possible to directly feed materials instead of through a small indoor heap, which significantly reduced Ni concentrations in the area. This reduction was well documented by the new sampling device, as was the differences between sites across the plant. This type of spatial evaluation has shown to be an integral part of the on-going work to reduce Ni emissions, that hopefully will contribute to lowering the total Ni concentrations in air surrounding the plant.

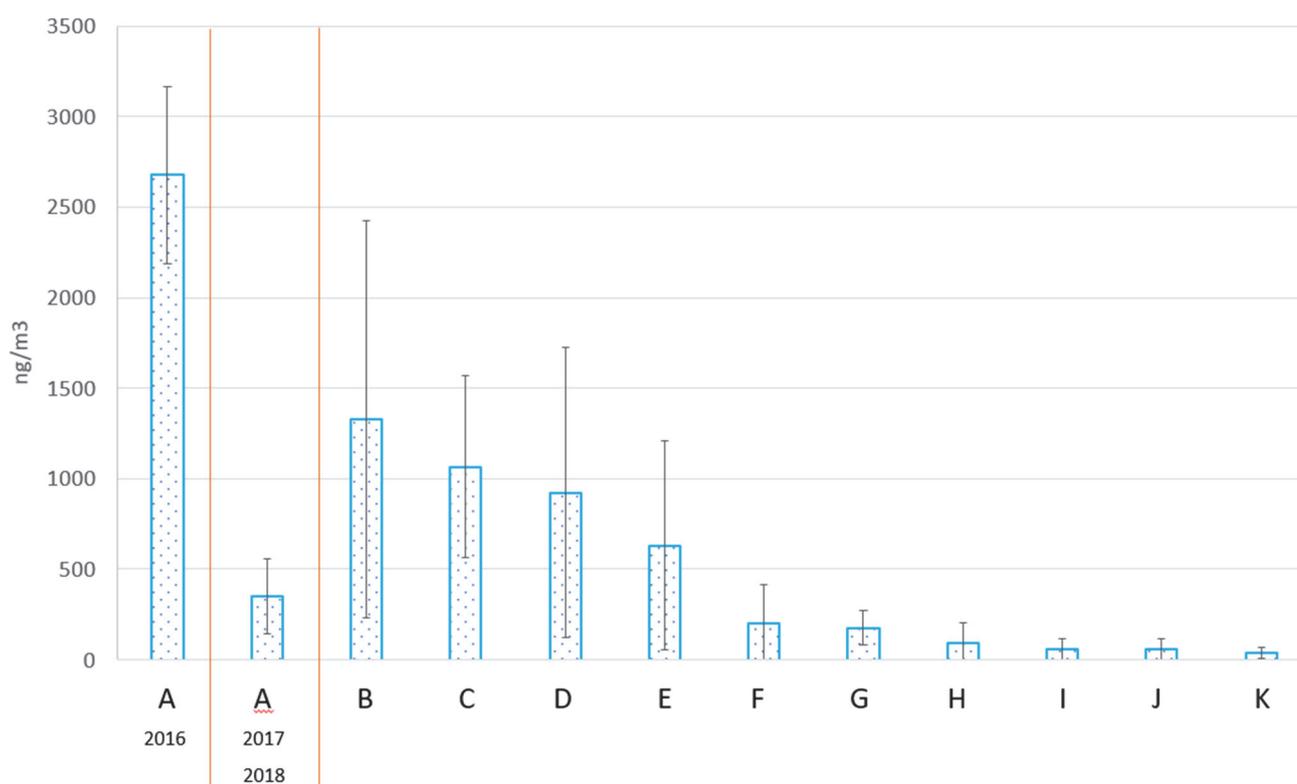


Figure 5. Average ambient Ni concentration with standard deviation for each measurement location. Two concentrations are given for location A, pre- and post-abatement of one source causing high Ni concentrations in an area.

Conclusion

The novel sampling device described in this work provides three equivalent filters that can be used to qualify filters for more extensive and parallel chemical analysis to investigate internal source contributions to ambient Ni concentrations within the plant area. The unit has been shown to operate very well according to all required functions and capabilities.

The Nikkelverk has used the results achieved through in-house Ni analysis of PM₁₀ filters in combination with process knowledge to do defensible investments that reduce Ni emission. The developed methodology helps to address three problems that inhibit the collection of co-located dust samples: cost, unknown Ni content of in collected dust (as they are not correlated), and

in the mobility of a sampling system for collecting co-located filters. If the methodology is to be developed into emission reporting type framework, a more detailed study with respect to TOS is required. Diffuse emission sources are heterogenous in nature and there is a question whether ambient sampling near sources can properly capture this.

The filter data base is going to be further analysed in a larger investigation into which sources specifically contribute most to the ambient Ni levels within plant fence lines. Samples with high Ni content are undergoing other advanced physicochemical analysis that can disclose specific sources going beyond just finding Ni hot spots. The characterization of the nickel compounds as sulphates, sulphides, chlorides etc. and the actual link to different process units is planned to be published later.

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