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FORUM FOR THEORY AND PRACTICE OF REPRESENTATIVE SAMPLING

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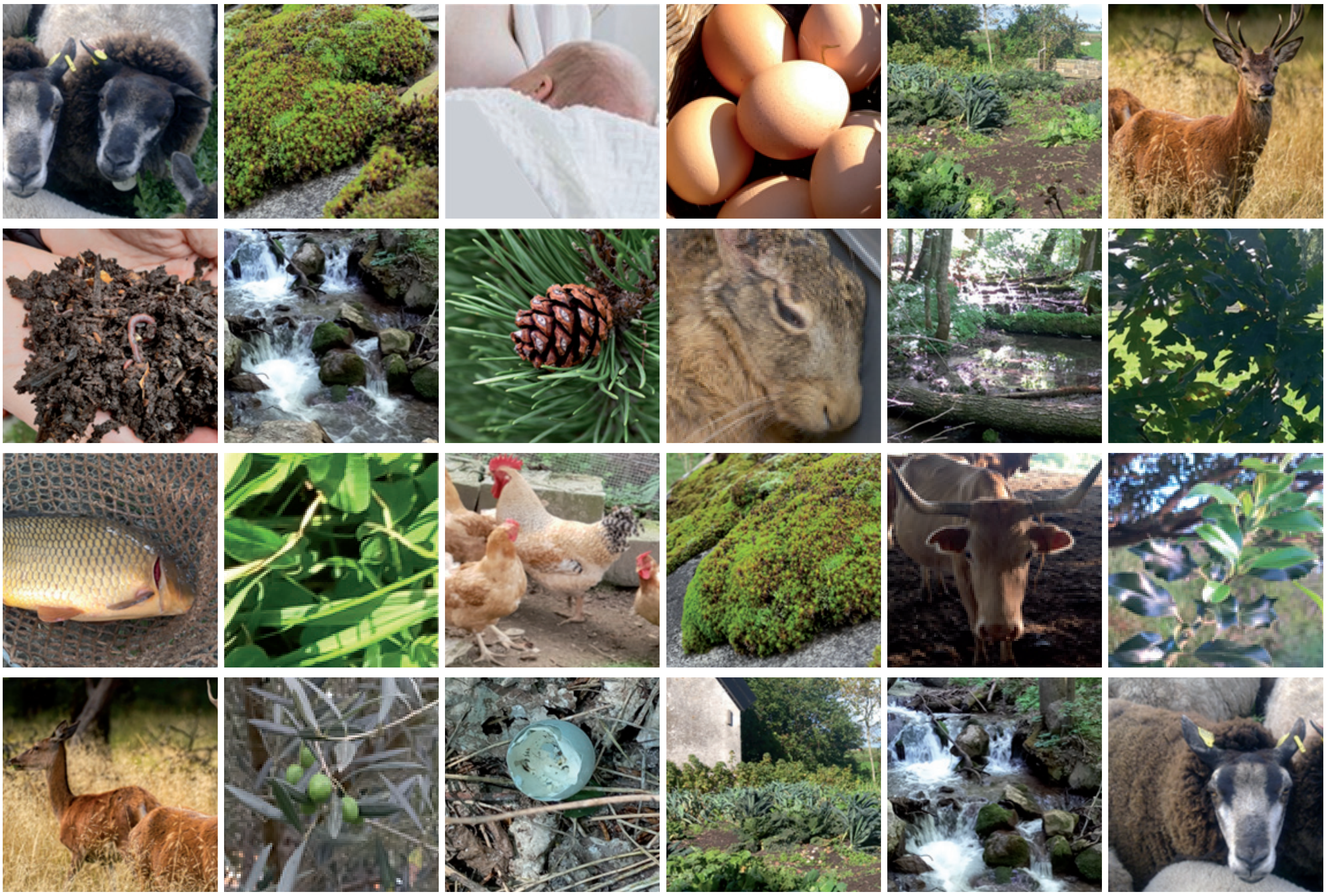
SAMPLING SCIENCE & TECHNOLOGY



Off-Broadway Sampling

New, Innovative and Exotic Sampling Media

Modelling the Liberation Factor
Pierre Gy's Approach

Heterogeneity characterization
The debate continues

Introducing the Theory of Sampling
Augmented scope and new didactics

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Cover Photo

Alternative sample media used in ToxicoWatch biomonitoring research.
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Off-Broadway Sampling

By Kim H. Esbensen (Editor)

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> ***Biomonitoring*** *involves the use of organisms to assess environmental contamination (pollution). Biomonitoring is carried out quantitatively by measuring accumulation of chemicals in organism tissues. By observing or measuring the effects the environment has on its resident organisms, suspected pollution can be indicated, demonstrated or proved. In analytical chemistry* ***biomonitoring*** *means measurement of the body burden of toxic chemical compounds, elements and or their metabolites in biological tissues. With the human perspective, such measurements are typically performed on blood and urine samples, but involving whole populations (or statistically selected parts hereof) often requires a major logistical and economic effort.* ***Biomonitoring*** *serves several purposes and objectives regarding environmental health, occupational safety, workplace health surveillance – and as a means of toxic pollution exposure assessment – the latter preferentially with a minimum economic cost in order to provide maximum coverage e.g. of threatened population segments or local communities living close to potential or* ***proved*** *sources of toxic emissions and related pollution.*
>
> *An* ***off-Broadway*** *theatre is an alternative professional venue in New York City with limited seating, distinctly different from the established big Broadway theaters. The term originally referred to any venue and its productions on a street intersecting Broadway Avenue in Midtown Manhattan's theater district, the center of the American theatre. An 'off-Broadway production' is a production (play, musical) appearing in such a venue. The present* ***off-Broadway SST issue*** *brings some not-so-mainstream sampling media to its readers!*

The Dutch Not-for-Profit organisation TOXICOWATCH has for ~15 years performed a critical and wide-ranging public duty on a shoestring budget - with remarkable technological, environmental, and societal impact.

For its **biomonitoring** fieldwork, TOXICOWATCH is developing a very broad range of sampling media (sample types in the TOS parlance) to do environmental assessments. TOXICOWATCH's new, innovative sampling media are of more than academic interest — indeed quite the contrary. This issue of SST is proud to present the prospects offered by this creative sampling media bonanza to the IPGSA community, an approach far removed from our more traditional sample types: rocks, ore, soil, food, feed, industrial intermediates, and final products. Indeed, we are introduced to the featured topic of SST#3 which the editor has termed '**Off-Broadway sampling**'.

The first two articles in this issue truly live up to this declaration. The first by TOXICOWATCH, which kindly accepted an invitation to feature its important societal work with a focused scope on the bewildering range of sampling media used. This is followed by an even more exotic approach for a purpose so far away from IPGSA's traditional sampling context so as to defy belief — at first. But it is hoped these clashes with our usual sampling approaches will be inspiring for the IPGSA community.

Two articles follow from the highest echelons re. sampling theory, complementing the featured theme in SST#2, '**Heterogeneity Testing**'. The debate that was initiated there is enfolding with élan and panache — to be appreciated here in SST#3 as well. This is a front-and-center debate on a perennial theme that has been discussed for many decades .... Will these two articles close this debate?

Alan Rawle continues his magisterial series 'Giants of Sampling' with a third contribution, this time on **Sylvanus Albert Reed**. We are again treated to a wonderful and colorful tour de force through a decisive life with ample achievement and impact, most certainly not only regarding sampling. Thank you, Alan, for enriching our collective historical education.

Finally, there is a new attempt at a most difficult subject: What is the *best way* to introduce the Theory of Sampling (TOS) to parties new to this discipline? There are currently several attempts to solve this challenge ongoing within IPGSA where the goal is to be able to explain the tenets of TOS in the clearest and simplest language possible. In the alternative attempt presented here, the author (who has more than 25 years educational experience) has decided to address an educated audience (general university education level). Why? Because, going forward, this is precisely where IPGSA will find its largest new audiences (still) not aware of the need for and the benefits to be had from TOS.

This issue concludes with three important association news messages. Enjoy SST#3!

Introduction of Innovative Sampling Media for Biomonitoring of Environmental Loads of Persistent Organic Pollutants (POPs)

By Abel Arkenbout[1], Kirsten Bouman[1] and Kim H. Esbensen[2]

DOI: 10.62178/sst.003.002

ABSTRACT

Combustion-related industry activity inevitably results in emissions of toxic substances, such as dioxins, PFAS, PAH, also called persistent organic pollutants (POPs) and heavy metals, with a key focus on to what degree this is accompanied by unacceptable pollution in the surrounding environments. Measurements of the environmental load of these and other industrial emissions are today limited in terms of relevant time frame, frequency and target POPs. A comprehensive systematic monitoring is critically needed to support endangered surrounding environments and the health of local populations. Here we present selected studies from the last decade developing a science-backed basis for improving monitoring of industrial emission deposition loads of hazardous POP substances with a special focus on the use of both conventional as well as *innovative* sampling media: soil, water, sediments, *sheep's wool*, *eggshells* of wildlife birds, mosses (*Bryophytes*), pine needles (*Picea abies; Pinus sylvestris*), evergreen tree leaves (*Olea europaea; Quercus ilex*), *liver* (from dead wildlife animals), even *mother's milk*. In this article we highlight some of the challenges involved in using this wide array of sampling media for biomonitoring with respect to representativity, reproducibility (practical monitoring), and relationship to the often highly advanced analytical methods employed. An important result of the work carried out by ToxicoWatch (TW) is that local communities become involved and are actively participating in the practical realisation of relevant research and monitoring projects. With this approach, local communities feel listened to and experience in practice that action is taken to focus their serious concerns through citizen-participation in scientific research and communication between polluting agents, governments, and other relevant organisations. In this way ToxicoWatch acts as a bridge between local communities, industry, and government.

1. Background – ToxicoWatch

European Union (EU) regulations concerning monitoring of industrial emissions of hazardous POP substances currently specify a monitoring frequency *only* amounting to one or two preannounced times yearly (monitoring periods six to eight hours per year (6-16 h/y) on a selected group of chlorinated dioxins (PCDD/F/dl-PCBs) and a limited number of heavy metals *only*, while the important group of other (mixed) halogenated POPs, such as brominated dioxins (PBDD/F), PFAS, mixed halogenated PAH, and chlorinated paraffins are currently *not* included in any mandated monitoring regulation.

Measurements for mandated monitoring of flue gasses are only performed during 'optimal production conditions', in stark contrast to firm evidence that POP emissions are mostly emitted during so-called 'calamities', such as start-ups/shut-downs, technical failures related to insufficiently high temperatures, and wet waste content. Besides such technical failures, toxic outputs without an optimum functioning filter system are a main source of industrial emissions into the surrounding environment according to current Best Available Techniques & Best Environmental Practices (BAT/BEP).

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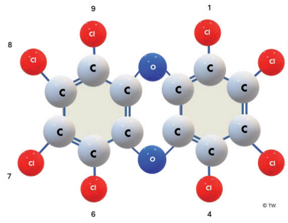
[2] KHE Consulting, Copenhagen, Denmark

What are dioxins?

Dioxins are formed by halogens: Chlorine (Cl=Chlorine) or other halogens (F=Fluorine, Br=Bromine, I=Iodine), or a mixture of halogens. These halogens are arranged on two benzene rings of carbon atoms (Carbon (C=Carbon), to which 1-8 chlorine or other halogen atoms may be attached. These rings are joined by 2 oxygen (O=Oxygen) atoms, "di-oxy". Furans have one oxygen (O) in the molecular compound and in the case of dl-PCBs, no oxygen (O) atom is present in the molecular compound.

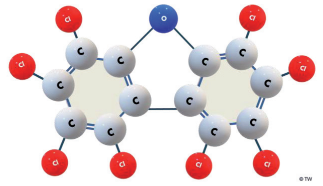
Dioxins are substances, by-products, unintentionally produced during thermal (industrial production) processes, such as waste or co-incineration. In this process, they are mainly formed during incomplete combustion (including low combustion temperatures < 850 C degrees for 2 seconds) incase of waste incineration. By cement kiln incineration with higher temperatures (1100-1600 C degrees), the risk of dioxins emissions occurs during the cool down phase. As well during the heath up in start-up phase waste material of high burning quality (PCB oil, plastics, old car tyers) might be used as well to secure the required high combustion temperatures needed for production of a cement kiln.

Dioxins are Unintentional formed Persistent Organic Pollutants (POPs), and therefore also called UPOPs



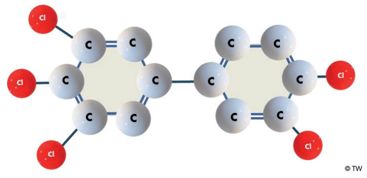
OctaChloroDibenzo-p(ara)-Dioxin (OCDD)

Dioxins PCDD
Polychlorinated dibenzo-p(ara) dioxin



OctaChloroDibenzoFuran (OCDF)

Furans PCDF
PolyChlorinated DibenzoFurans



Dioxin-like PCB 126

Dioxin-like PCB (dl-PCB)
PolyChlorinated Biphenyl

Credit: ToxicoWatch; used with permission.

Figure 1: What are dioxins?

In 2019, stricter regulations for waste incinerators were established regarding emissions of POPs in Europe (Neuwahl et al.,2019). However, a glaring loophole to avoid these restrictions is the exemption for permits given before 2019. Thus, 'old' incinerators can still emit high levels of POPs due to these permits. Even new, recently built waste incinerators can get 'off the hook' due to governmental accordance with permits allowed *before* 2019. One of the oldest and largest waste incinerators in Paris, Ivry Paris XIII, which has been operating since 1969, started to be rebuilt in 2024 to modernise the technical equipment and transform the plant into a state-of-the-art Waste-to-Energy (WtE) waste incinerator – but its operation is *still* based on a permit *before* 2019. Although there are various worldwide regulations in play, the major problem is accurate and *transparent* enforcement based on specific knowledge of the targeted POPs.

One of the critical issues for emission control concerns monitoring the deposition of combustion-related industry aerial outputs to the surrounding environment(s). There is a critical need that monitoring of polluting entities be performed by *independent* organisations. This means not being connected to the specific industry branch involved, nor to enforcing government agencies.

In the last two decades, it has become clear that there is insufficient specific knowledge in governmental and enforcement organisations about *which*, and in *what quantity* POP loads are threatening the health of local communities living in the surrounding regions of POP emitting industries. Perhaps not surprisingly what has been revealed – over many decades – are (far) too laxed attitudes towards monitoring conditions (duration, frequency, targeted POPs).

To contribute towards filling this gap, ToxicoWatch (TW), a Public Benefit Organisation, has initiated and continues to develop a science-backed, fully documented biomonitoring approach with which to characterise and measure emissions of dioxins, PFAS, PAH, and heavy metals in the surrounding environment of POP emitting industries. In this article several cases are presented showing how current TW biomonitoring research contribute to informative, transparent documentation and characterisation of POP pollution in the environment. Within this scope, this article has a particular focus on the many kinds of new *innovative sampling media* that has been found useful for this type of biomonitoring research projects.

2. Why is Biomonitoring needed?

Human society is increasingly confronted with pollutants that are persistent, bioaccumulative and extremely toxic, even at very low concentrations. Dioxins, dioxin-like PCBs and PFAS present a significant challenge to human health due to their hormonal effects. Waste incinerators are equipped with comprehensive Air Pollution Control Devices (APCD) designed to eliminate air pollution. However, it should be noted that emissions may occur during emergency situations, when the functionality of these devices may not be fully optimised. These periods are often very short, and even with semi-continuous measurements, it can be challenging to capture them accurately (Arkenbout et al., 2018). Considering this, it may be beneficial to implement structural biomonitoring into the existing monitoring regime, in addition to regular chimney emissions measurements. Biomonitoring, which involves measuring these highly toxic environmental pollutants in various biological media such as eggs of backyard chicken, cow/sheep milk and vegetation, could provide a more comprehensive overview of actual accumulated emissions to the environment. This approach can offer a better understanding of the ongoing POP-emissions, as opposed to a brief measurement in the chimney under ideal conditions.

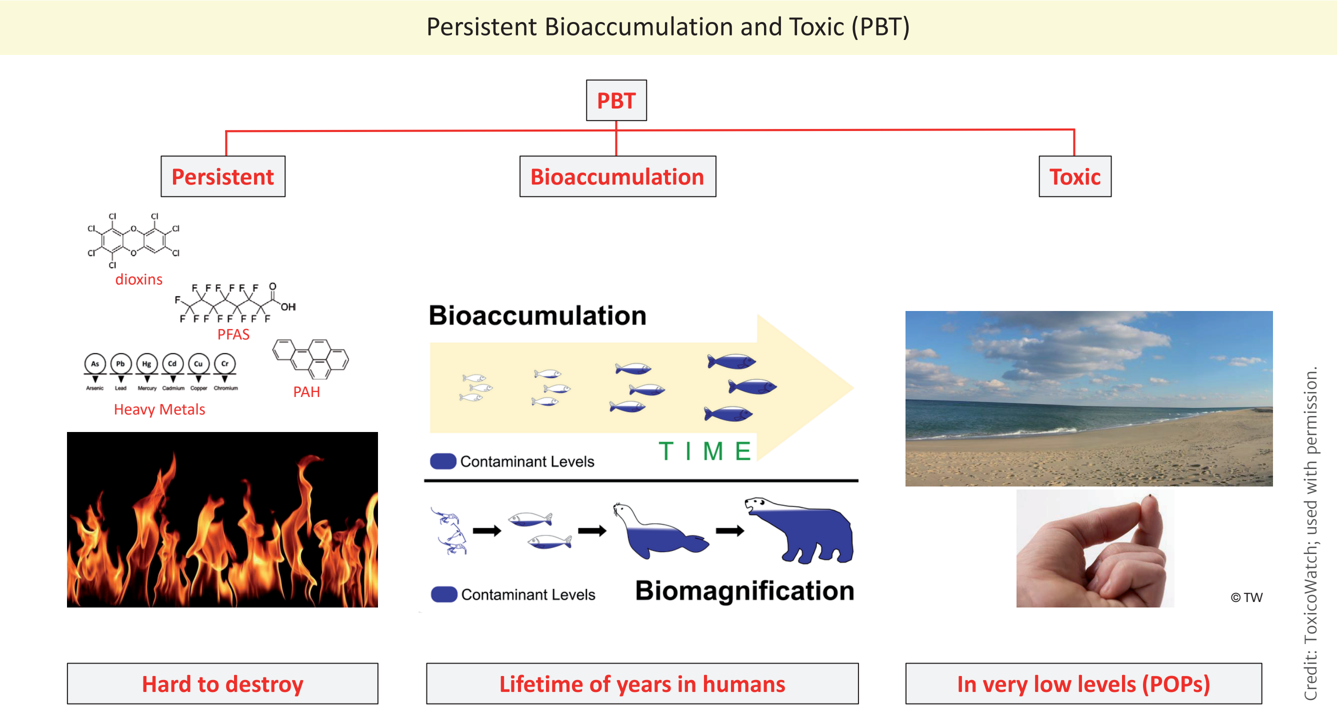
These Substances of Very High Concern (SVHC) degrade only very slowly, for which reason they are aptly called ‘forever chemicals. Once produced/released/emitted, they remain present in the environment for years, decades, or longer – and *some* toxic substances stay in the human body for life.

3. TWs first biomonitoring initiatives (2013)

In 2013 TW initiated a biomonitoring research program in the surrounding area of the most recent Waste-to-Energy (WtE) incinerator in the Netherlands, REC, operated since 2011. The study focused on the issue of *dioxins occurring in the surrounding environment of this state-of-the-art WtE incinerator*.

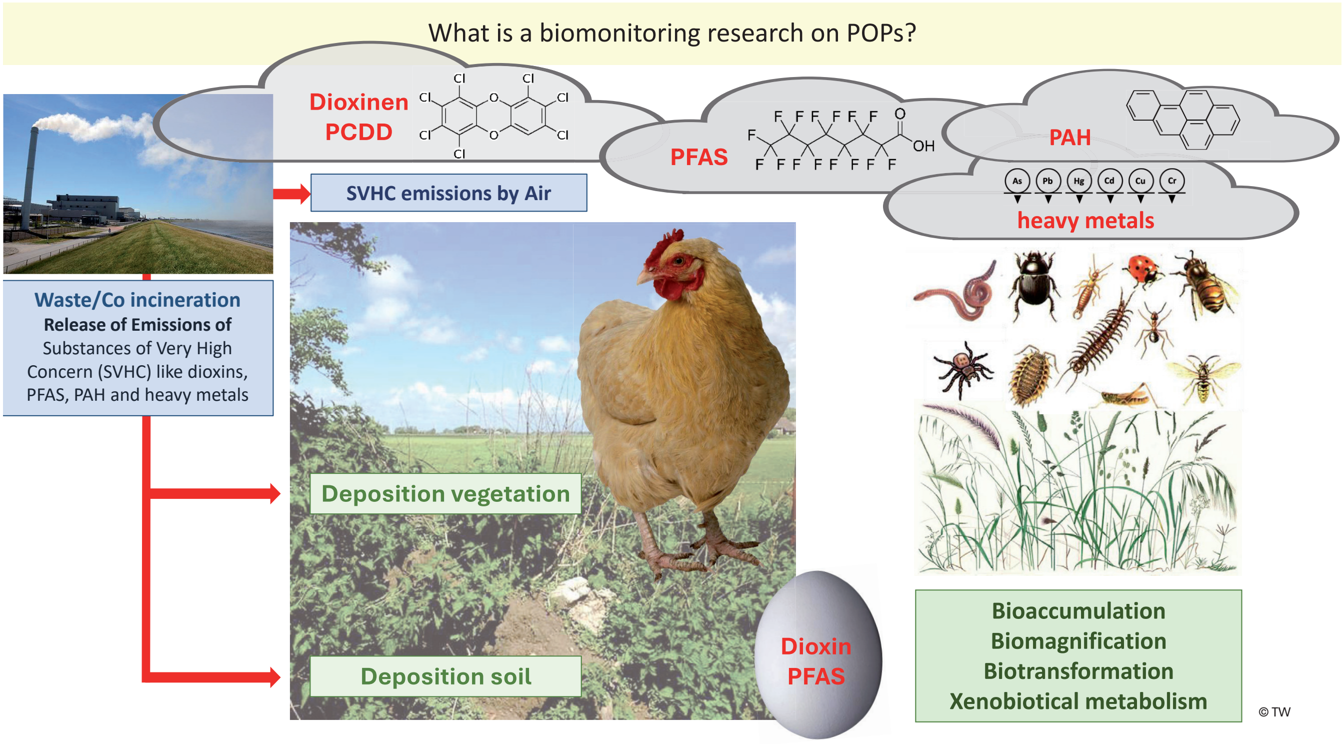
3.1 ToxicoWatch’s first innovative sampling medium

The first biomonitoring research by ToxicoWatch in 2013 was focused on innovative use of backyard chicken eggs from private chicken coop owners living nearby as a novel sampling medium. There are several challenges for using such a bioaccumulating medium, which is subject to *biomagnification*, *biotransformation*, and *xenobiotic metabolism*.



Credit: ToxicoWatch; used with permission.

Figure 2: Key properties (Persistent-Bioaccumulation-Toxic) of Substances of Very High Concern (SVHC)



Credit: ToxicoWatch; used with permission.

Figure 3: The setting of the use of the novel sampling medium backyard chicken eggs for measuring pollution loads of dioxins, PFAS and heavy metals.

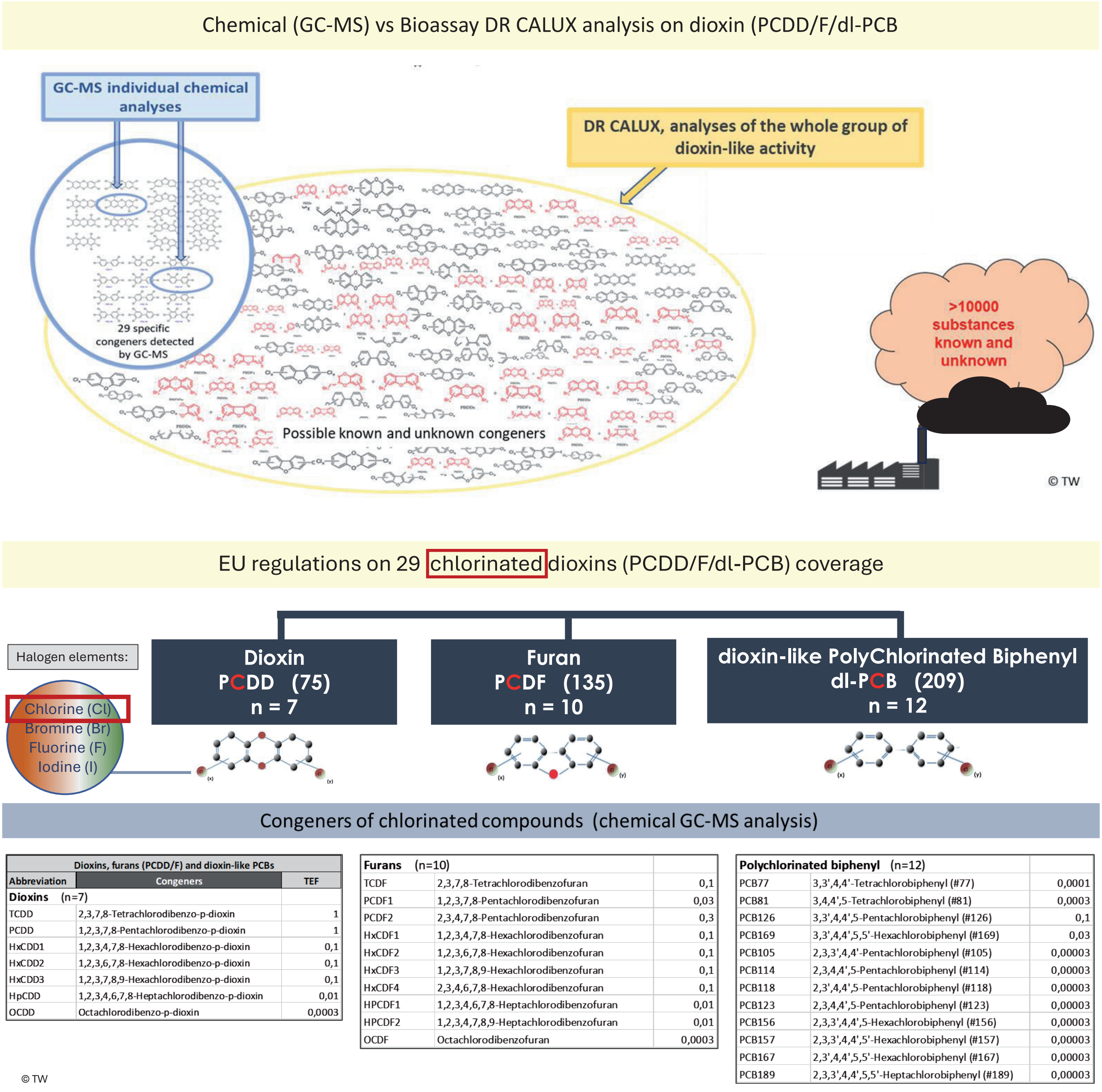
While critical for the scientific understanding of biomonitoring, these analytical aspects are not treated in full here, as ToxicoWatch has discussed these challenges extensively elsewhere in the literature and at relevant scientific conferences (Jovan et al., 2024; Musilova et al., 2024; Qarri et al., 2019; Arkenbout & Esbensen, 2017), see chapter 3.2.

3.2 Bioaccumulation, biomagnification, xenobiotic metabolism

Within the domain of sampling-for-analysis, biomonitoring presents a series of complex challenges regarding the specific analytes used for quantifying deposition load. Whereas most objectives involving sampling organised within the IPGSA community are aimed at analysis and quantification of simple, singular analytes, which are (relatively) easy to quantify e.g., base metals, heavy metals, precious metals, rare earth elements (REE), mineral commodities, food and feed components. Biomonitoring involves quantifying more complex ‘analytes’, many of which are subject to potential forms of interference in the form of bioaccumulation, biomagnification, and xenobiotic metabolism.

3.3 DR CALUX

The DR CALUX (Dioxin-Responsive Chemical Activated LUciferase gene eXpression) bioassay is a specialized assay used to detect and quantify dioxins, dioxin-like compounds, and other related environmental pollutants. It is based on the use of genetically engineered cell lines that contain a luciferase reporter gene under the control of a dioxin-responsive element. When these cells are exposed to dioxins or dioxin-like compounds, the compounds bind to the aryl hydrocarbon receptor (AhR) within the cells, which then activates the transcription of the luciferase gene. The key features of the DR CALUX bioassay include Sensitivity: The assay is highly sensitive, allowing for the detection of very low concentrations of different types of halogenated dioxins and related compounds. Quantitative Measurement: The amount of light emitted by the luciferase reaction is proportional to the concentration of dioxins present, enabling quantification of these compounds. High Throughput: The assay can be performed in a high-throughput format, making it suitable for screening large numbers of samples quickly and efficiently. Environmental and Food Safety Applications: The DR CALUX bioassay is widely used in environmental monitoring and food safety testing to assess contamination levels of dioxins and similar compounds in various matrices, including soil, water, air, and food products. Generally, the DR CALUX bioassay is an important tool for assessing the presence and potential risk of dioxins and related pollutants in the environment and food supply. CALUX bioassays are novel approaches to fill the data gaps between chemical analyses and the total toxicity of mixtures of substances.



Dioxins, furans (PCDD/F) and dioxin-like PCBs		
Abbreviation	**Congeners**	**TEF**
Dioxins (n=7)		
TCDD	2,3,7,8-Tetrachlorodibenzo-p-dioxin	1
PCDD	1,2,3,7,8-Pentachlorodibenzo-p-dioxin	1
HxCDD1	1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	0,1
HxCDD2	1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	0,1
HxCDD3	1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	0,1
HpCDD	1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	0,01
OCDD	Octachlorodibenzo-p-dioxin	0,0003

Furans (n=10)		
TCDF	2,3,7,8-Tetrachlorodibenzofuran	0,1
PCDF1	1,2,3,7,8-Pentachlorodibenzofuran	0,03
PCDF2	2,3,4,7,8-Pentachlorodibenzofuran	0,3
HxCDF1	1,2,3,4,7,8-Hexachlorodibenzofuran	0,1
HxCDF2	1,2,3,6,7,8-Hexachlorodibenzofuran	0,1
HxCDF3	1,2,3,7,8,9-Hexachlorodibenzofuran	0,1
HxCDF4	2,3,4,6,7,8-Hexachlorodibenzofuran	0,1
HPCDF1	1,2,3,4,6,7,8-Heptachlorodibenzofuran	0,01
HPCDF2	1,2,3,4,7,8,9-Heptachlorodibenzofuran	0,01
OCDF	Octachlorodibenzofuran	0,0003

Polychlorinated biphenyl (n=12)		
PCB77	3,3',4,4'-Tetrachlorobiphenyl (#77)	0,0001
PCB81	3,4,4',5-Tetrachlorobiphenyl (#81)	0,0003
PCB126	3,3',4,4',5-Pentachlorobiphenyl (#126)	0,1
PCB169	3,3',4,4',5,5'-Hexachlorobiphenyl (#169)	0,03
PCB105	2,3,3',4,4'-Pentachlorobiphenyl (#105)	0,00003
PCB114	2,3,4,4',5-Pentachlorobiphenyl (#114)	0,00003
PCB118	2,3',4,4',5-Pentachlorobiphenyl (#118)	0,00003
PCB123	2,3,4,4',5-Pentachlorobiphenyl (#123)	0,00003
PCB156	2,3,3',4,4',5-Hexachlorobiphenyl (#156)	0,00003
PCB157	2,3,3',4,4',5'-Hexachlorobiphenyl (#157)	0,00003
PCB167	2,3',4,4',5,5'-Hexachlorobiphenyl (#167)	0,00003
PCB189	2,3,3',4,4',5,5'-Heptachlorobiphenyl (#189)	0,00003

Credit: ToxicoWatch; used with permission.

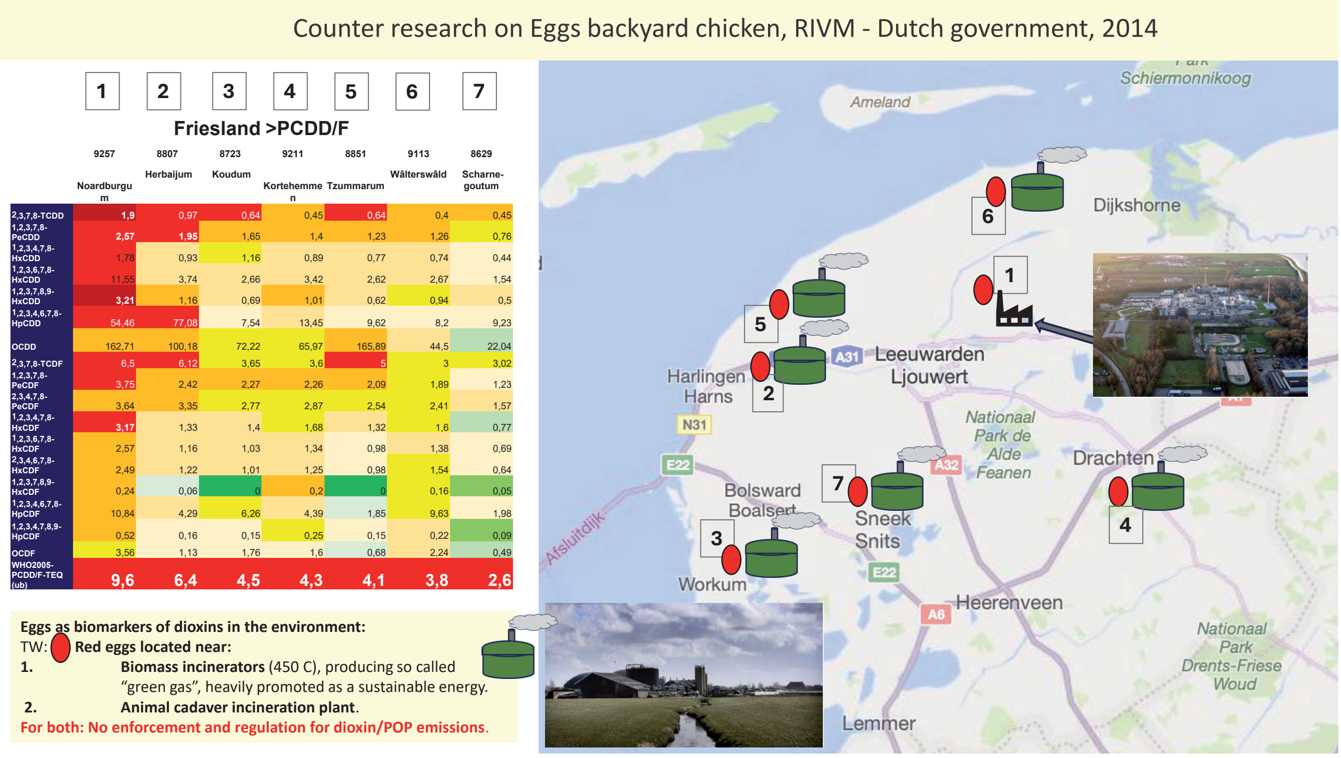
Figure 4: Chemical analysis of 29 chlorinated compounds vs bioassay DR CALUX measures a more comprehensive total toxicity of dioxins, not only the EU-regulated 29 chlorinated congeners.

The chemical analysis is based on a limited number of congeners of 29 chlorinated dioxins. CALUX bioassays measure the *biological effect* of a whole *group of toxic substances*. In addition, TW also uses other bioassays, like the PFAS CALUX, which is based on the binding to the thyroid transporter receptor, TTR.

4. First (now famous) results based on backyard chicken eggs

Analytical results of dioxins (PCDD/F/dl-PCBs) in eggs have led to extensive follow-up, and to counter-research by the Dutch Governmental health organisations and industry. For more than two years TW became the sole independent member (representing the concerned population) of the technical working group assembled by delegates of provincial governments and industry/REC management. From activities in a technical work group established by the government and the incinerator plant management, a lot of technical data on emissions of the flue gasses were generated. Remarkably, frequent high dioxin emissions were detected due to technical imperfections in the air pollution control devices (APCD). The outcome of these studies showed that biomonitoring is an essential tool to quantify *realistic loads* of POP deposition in the environment of combustion-related industry.

Counter research on Eggs backyard chicken, RIVM - Dutch government, 2014



Friesland >PCDD/F

	1	2	3	4	5	6	7
	9257	8807	8723	9211	8851	9113	8629
	Noardburgum	Herbaijum	Koudum	Kortehemmen	Tzummarum	Wâlterswâld	Scharnegoutum
2,3,7,8-TCDD	1,9	0,97	0,64	0,45	0,64	0,4	0,45
1,2,3,7,8-PeCDD	2,57	1,95	1,65	1,4	1,23	1,26	0,76
1,2,3,4,7,8-HxCDD	1,78	0,93	1,16	0,89	0,77	0,74	0,44
1,2,3,6,7,8-HxCDD	11,55	3,74	2,66	3,42	2,62	2,67	1,54
1,2,3,7,8,9-HxCDD	3,21	1,16	0,69	1,01	0,62	0,94	0,5
1,2,3,4,6,7,8-HpCDD	54,46	77,08	7,54	13,45	9,62	8,2	9,23
OCDD	162,71	100,18	72,22	65,97	165,89	44,5	22,04
2,3,7,8-TCDF	6,5	6,12	3,65	3,6	5	3	3,02
1,2,3,7,8-PeCDF	3,75	2,42	2,27	2,26	2,09	1,89	1,23
2,3,4,7,8-PeCDF	3,64	3,35	2,77	2,87	2,54	2,41	1,57
1,2,3,4,7,8-HxCDF	3,17	1,33	1,4	1,68	1,32	1,6	0,77
1,2,3,6,7,8-HxCDF	2,57	1,16	1,03	1,34	0,98	1,38	0,69
2,3,4,6,7,8-HxCDF	2,49	1,22	1,01	1,25	0,98	1,54	0,64
1,2,3,7,8,9-HxCDF	0,24	0,06	0	0,2	0	0,16	0,05
1,2,3,4,6,7,8-HpCDF	10,84	4,29	6,26	4,39	1,85	9,63	1,98
1,2,3,4,7,8,9-HpCDF	0,52	0,16	0,15	0,25	0,15	0,22	0,09
OCDF	3,56	1,13	1,76	1,6	0,68	2,24	0,49
WHO2005-PCDD/F-TEQ (ub)	**9,6**	**6,4**	**4,5**	**4,3**	**4,1**	**3,8**	**2,6**

Eggs as biomarkers of dioxins in the environment:
TW: ● **Red eggs located near:**
1. **Biomass incinerators** (450 C), producing so called “green gas”, heavily promoted as a sustainable energy.
2. **Animal cadaver incineration plant**.

For both: No enforcement and regulation for dioxin/POP emissions.

Credit: ToxicoWatch; used with permission.

Figure 5: Map of locations of RIVM, governmental counter-research of backyard chicken eggs in relation to dioxins (PCDD/F (based on Hoogenboom, RLAP, 2016).

In Europe, although *some* waste incinerators are followed by *limited* biomonitoring, industry unfortunately interferes with this research. Thus, a related study by the Dutch government found elevated dioxins in chicken eggs in *other places* than around the targeted incinerator. First after a legal process lasting two years was TW permitted insight regarding the location of the data obtained by this counter-research, which pointed to potential other dioxin sources, such as *biomass incinerators*. These so-called ‘green’ biomass waste incinerators act under a much lighter enforcement policy than regular waste incinerators. Biomass plants provide an alternative route for waste deposition. For example, in the Netherlands, a waste incinerator is not allowed to burn impregnated garden wood. The population must pay a fee for discarding impregnated garden fences when brought to municipal collection points, but the treatment of processed/impregnated garden wood is worrisome. According to a municipal spokesperson, treated wood (mostly containing Wolman salts with 2,4-Dinitrophenol, Sodium arsenate, Sodium chromate, and Sodium fluoride) must be delivered to such designated biomass incinerators. But here it is incinerated at *much too low temperatures* in incinerators, which are equipped with much *less efficient* filter systems that in units aimed to destroy the so-called ‘Substances of Very High Concern’ (SVHC).

5. Pushback

Monitoring with private backyard poultry eggs runs a high risk of adverse interpretation and pushback reactions. In several countries, large-scale media campaigns, run by government agencies, discourage local population from consuming (their own) chicken eggs. Whereas TW employs biomonitoring of backyard chicken eggs as a cost-effective way of measuring air pollution, the government‘s response places the problem of toxic load on the shoulders of the public. However, the fair intention should be for the relevant government agencies to take measures to identify the *source of pollution* and to *eliminate* or *reduce* unacceptable industrial emissions of hazardous substances. To set the pushback situation it its right perspective we have emphatically stated: “This is not an *egg* problem, but a *pollution* problem.”

Below we illustrate the benefits and associated challenges of TW’s significantly extended armament of analytic methods, conventional and novel/innovative, targeted and tailored for specific needs.

FACTBOX - Analytical challenges

Sampling biomatrices is not a simple, direct matter. Even sampling of backyard chicken eggs needs to be performed carefully, picking the eggs must be done by the research team first, and/or by TW trained local citizen-participants. It is necessary to perform location inspections before and after sampling, and to conduct a questionnaire interview of the participants involved to avoid interfering factors. TW conducts intensive trainings for this purpose.

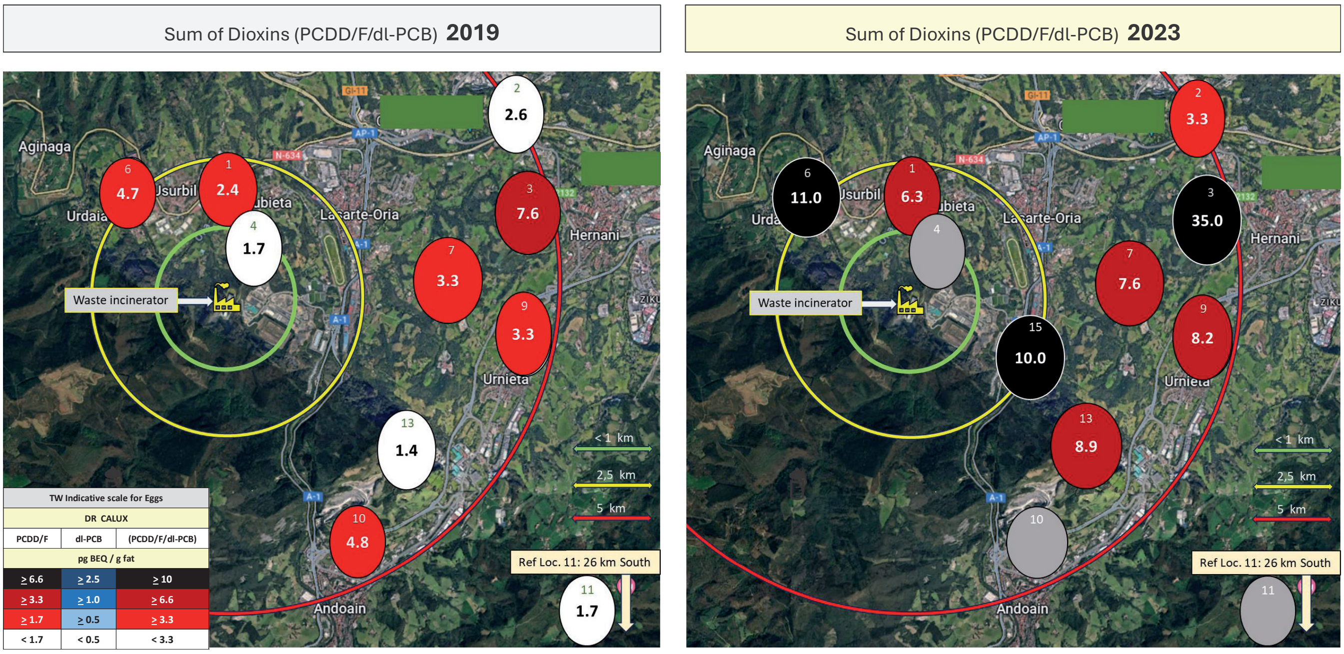
Additionally, TW uses mosses from the plant division *Bryophytes*, mostly identified as *Hylocomium splendens* and *Pleurozium schreberi* (local help from professional bryologists is always helpful for specific determination). All mosses, as well lichens, are extremely sensitive to air pollution, for which reason this biomarker is potentially very helpful for TW biomonitoring. In TW's studies, mosses appear to be able to accumulate POPs rapidly; likewise, when toxic waste is discontinued they detox quickly. How the dynamics of xenometabolism is functioning and how the various POPs are taken up is an area of current research.

Credit: ToxicoWatch; used with permission.

Figure 6: Complete array of conventional and novel ToxicoWatch biomonitoring sampling media tested in 2013-2025.

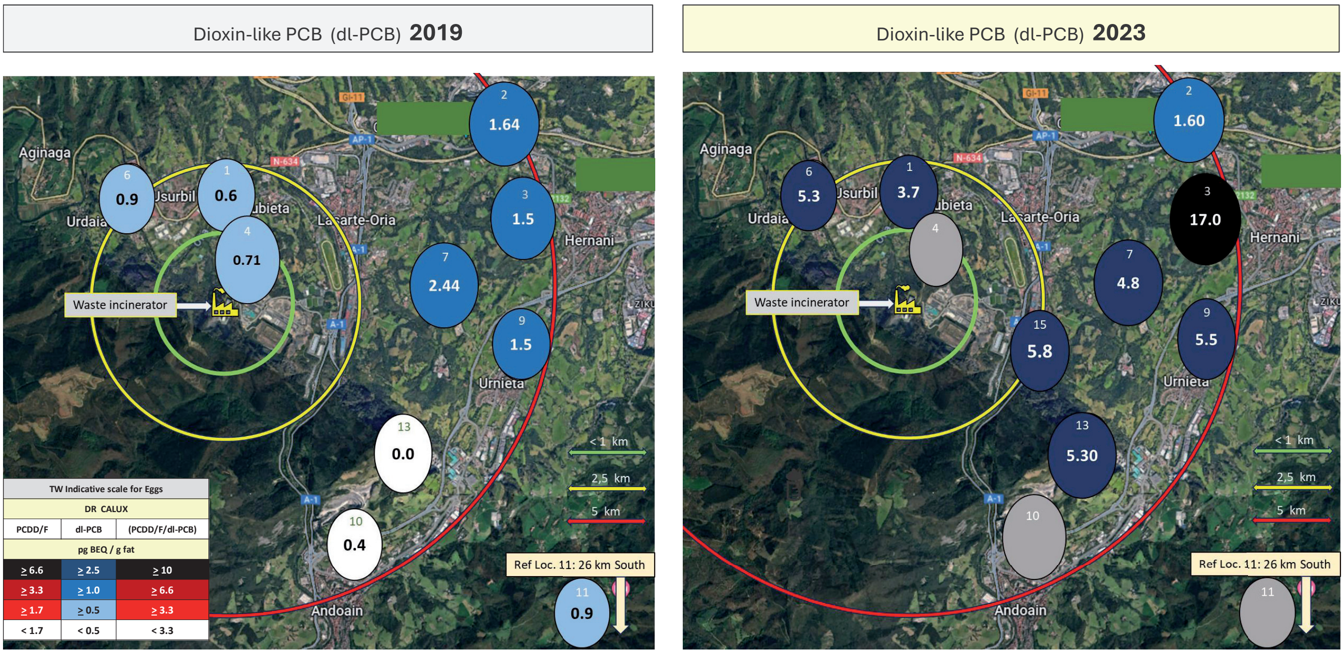
6. Innovative bioassay analyses and a broad spectrum of biomatrices for biomonitoring

Following up on the rationale behind the chicken egg approach, TW has further developed many other innovative bioassay analyses for expressing biomarkers to quantify industrial POP emissions. A selection of corresponding sampling media are illustrated in this article: soil, water, sediments, *sheep's wool*, *eggshells* of wildlife birds, mosses (*Bryophytes*), pine needles (*Picea abies; Pinus sylvestris*), evergreen tree leaves (i.e., *Olea europaea*) *liver* (from dead wildlife animals), *mother's milk*. For selected samples, the practical sampling procedures are shown. Figure 6 illustrates the wide range of biomonitoring sampling media that has been tested by Toxicowatch since 2013, see Figure 6 regarding the associated analytical challenges.



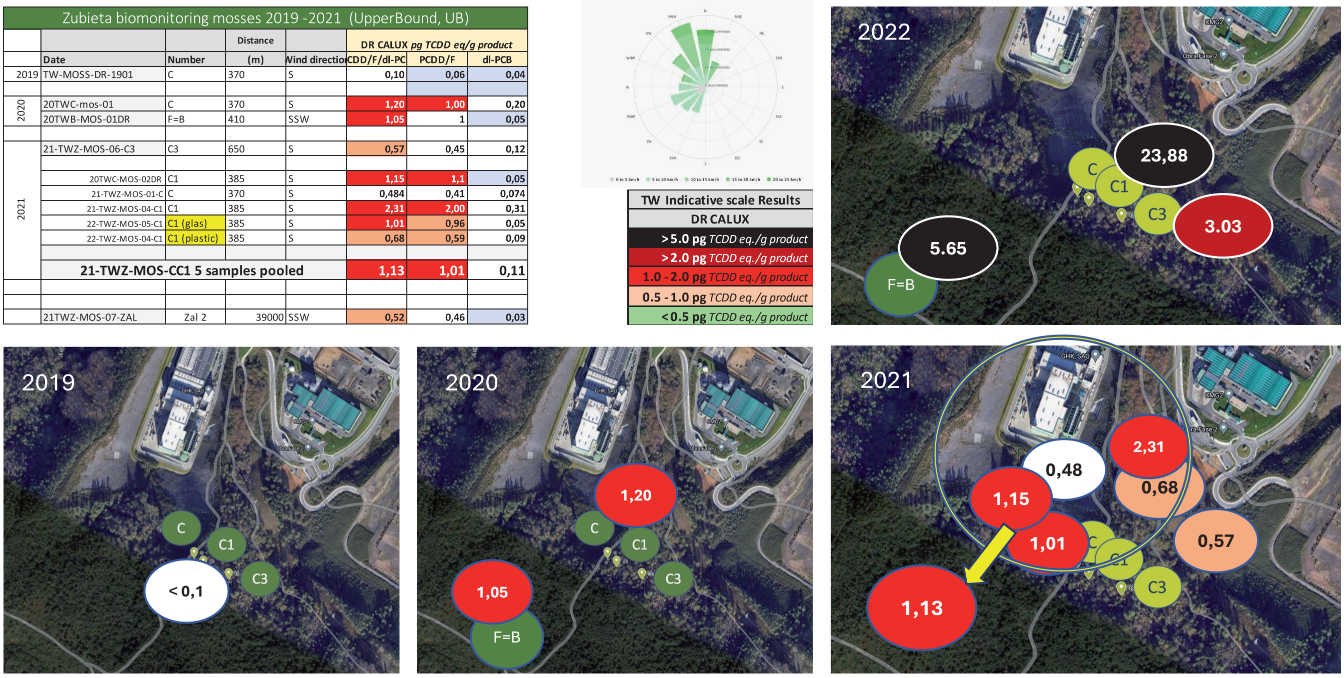
Credit: ToxicoWatch; used with permission.

Figure 7: Sum of dioxins (PCDD/F/dl-PCB) results with bioassay DR CALUX in eggs of backyard chicken, Zubieta, Basque country. 'Zero-measurements' in 2019 compared to the results five year later in 2023.



Credit: ToxicoWatch; used with permission.

Figure 8: Results dioxin-like (PCBs) with bioassay DR CALUX on eggs of backyard chicken. Comparison of zero-measurements (2019) and five years later in 2023 in the same locations.



Zubieta biomonitoring mosses 2019 -2021 (UpperBound, UB)

			Distance		DR CALUX *pg TCDD eq/g product*		
	Date	Number	(m)	Wind directio	CDD/F/dl-PC	PCDD/F	dl-PCB
2019	TW-MOSS-DR-1901	C	370	S	0,10	0,06	0,04
2020	20TWC-mos-01	C	370	S	1,20	1,00	0,20
	20TWB-MOS-01DR	F=B	410	SSW	1,05	1	0,05
2021	21-TWZ-MOS-06-C3	C3	650	S	0,57	0,45	0,12
	20TWC-MOS-02DR	C1	385	S	1,15	1,1	0,05
	21-TWZ-MOS-01-C	C	370	S	0,484	0,41	0,074
	21-TWZ-MOS-04-C1	C1	385	S	2,31	2,00	0,31
	22-TWZ-MOS-05-C1	C1 (glas)	385	S	1,01	0,96	0,05
	22-TWZ-MOS-04-C1	C1 (plastic)	385	S	0,68	0,59	0,09
	21-TWZ-MOS-CC1 5 samples pooled				**1,13**	**1,01**	**0,11**
	21TWZ-MOS-07-ZAL	Zal 2	39000	SSW	0,52	0,46	0,03

TW Indicative scale Results
DR CALUX
> 5.0 pg *TCDD eq./g product*
> 2.0 pg *TCDD eq./g product*
1.0 - 2.0 pg *TCDD eq./g product*
0.5 - 1.0 pg *TCDD eq./g product*
< 0.5 pg *TCDD eq./g product*

Figure 9: Results for dioxins (PCDD/F) in Mosses (Bryophytes), Zubieta, Basque Country 2019-2022.

Credit: ToxicoWatch; used with permission.

7. Selected application cases of dioxin results

Since the start of TW biomonitoring activities in 2013, TW has carried out intensive research in seven European countries; most of these studies are multi-year study projects. Selected illustrative studies are presented here below.

Waste incinerator, Zubieta, Basque Country, Spain

In 2019, TW started a so-called 'zero measurement' experiment in the environment of Zubieta, located in the North of Spain, The Basque Country. This is called a 'zero measurement' study because a year later in 2020 a newly built Waste-to-Energy (WtE) waste incinerator would go into production and therefore TW had the unique opportunity to collect environmental POP data *before* industrial emissions would begin. Concerned local communities contacted TW in 2019 to help with biomonitoring by collecting data on dioxins, PAH, PFAS and heavy metals from the following sampling media (biomatrices): i) backyard chicken eggs, ii) vegetation, iii) water, iv) sediment, v) soil and vi) mother's milk. Every year since 2019, samples have been collected at the same locations in this Basque area. This resulted in data that can be used to monitor the temporal evolutions of POPs in the surrounding environment of the waste incinerator.

Figure 7 shows the analytical results for the sum of dioxins (PCDD/F/dl-PCB) in eggs in the vicinity of the newly built waste incinerator. The first year 2019 established the zero-measurement baseline; these relatively low values are shown on the left in Figure 7. A year later, in 2020, the new incinerator was in full production. Elevated dioxins can already be found in the chicken eggs, but after 5 years, in 2023, the amounts of dioxins have increased dramatically, Figure 7 (right).

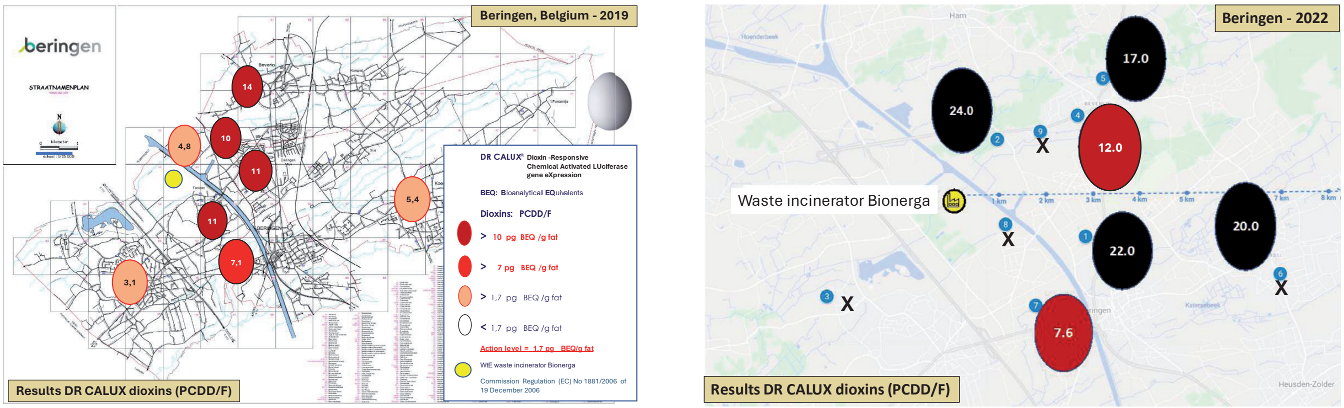
Figure 8 compares the presence of dioxin-like PCB (dl-PCBs) in 2019 and 2023 from the same localities near the waste incinerator in Zubieta, Basque Country. Since the 1970s PCBs have been banned, and it is therefore worrying to measure an increase of these toxic substances after ca. 50 years.

Close to this Zubieta WtE incinerator, mosses (*Bryophytes*) were also collected and analysed for dioxins. Figure 9 shows an example of evolution of dioxin levels in the mosses in the vicinity of the newly built (2020) waste incinerator between 2019-2022: The moss samples (C & B in Figure 9) were collected from the ground 300-500 meters south-west from the incinerator.

7.1 Waste incinerator Bionerga in Beringen, Belgium

In 2019 TW started similar zero-measurements of POP in the surrounding environment of a newly built WtE incinerator Bionerga in Beringen, Belgium, which started production in 2020. The concerned local population, represented by “Leefbaar Tervant”, convinced the local government to perform TW biomonitoring for three years (2019-2021/2022) on dioxins (PCDD/F/dl-PCB) in eggs of backyard chicken (Arkenbout & Bouman, 2023). Although the zero measurements already show elevated dioxin values in the backyard chicken eggs in this industrialised area, what is remarkable is the finding of high, significantly above EU-threshold dioxin levels found in the chicken eggs in 2022 (compare with Figure 11).

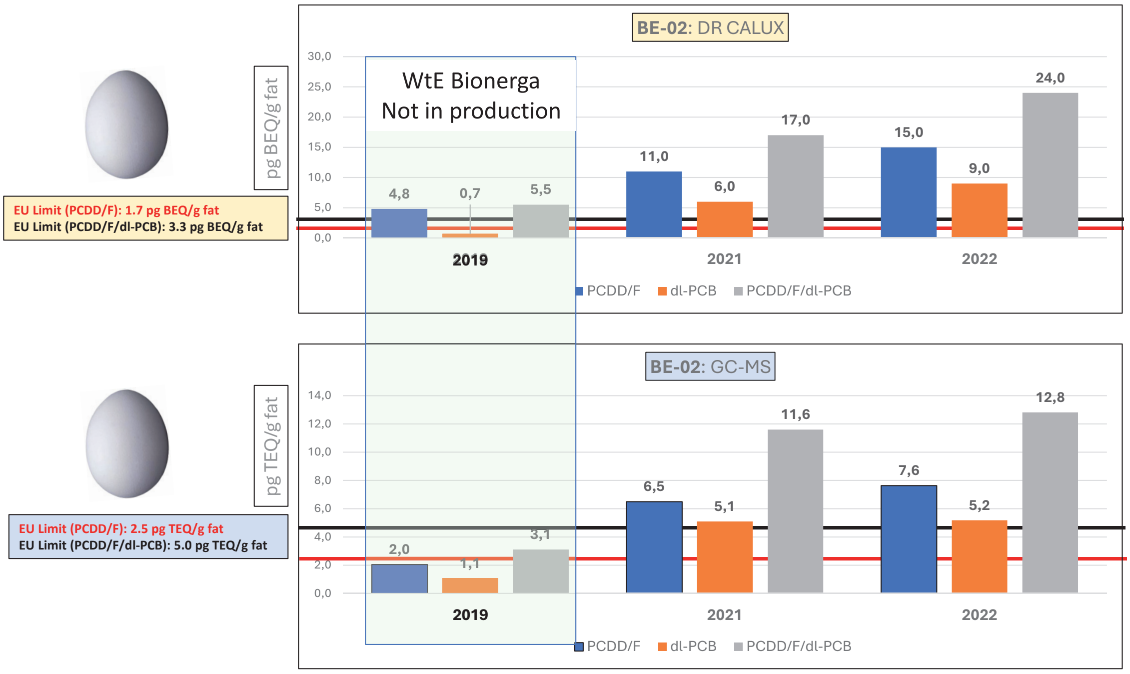
Results Dioxins (PCDD/F) in eggs of backyard chicken, Beringen, Belgium 2019-2022



Credit: ToxicoWatch; used with permission.

Figure 10: Results of dioxins (PCDD/F/dl-PCBs) in eggs of backyard chicken, Beringen, Belgium, which started with zero-measurement 2019 compared to three years later 2022.

EU Limit for Dioxins (PCDD/F) in eggs of backyard chicken, Beringen, Belgium 2019-2022

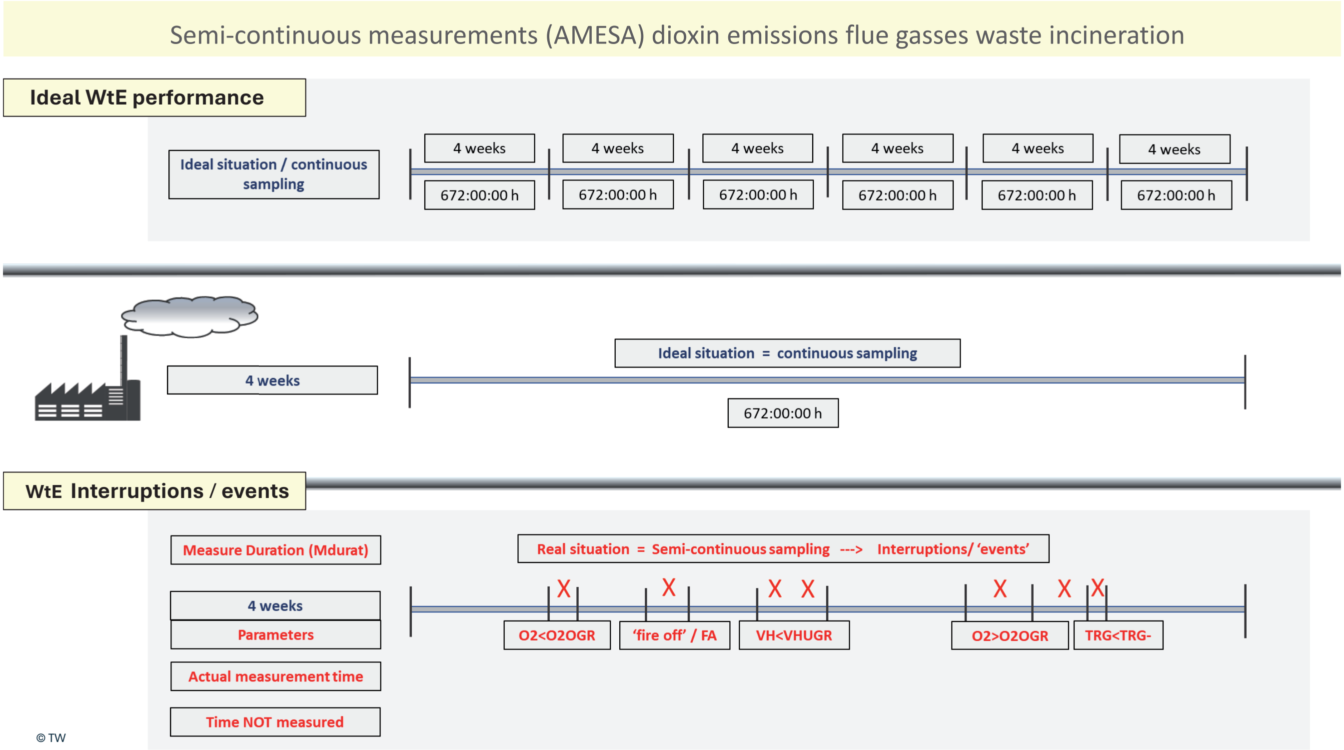


Credit: ToxicoWatch; used with permission.

Figure 11: EU limit for dioxins in backyard chicken eggs, Beringen, Belgium 2019-2022.

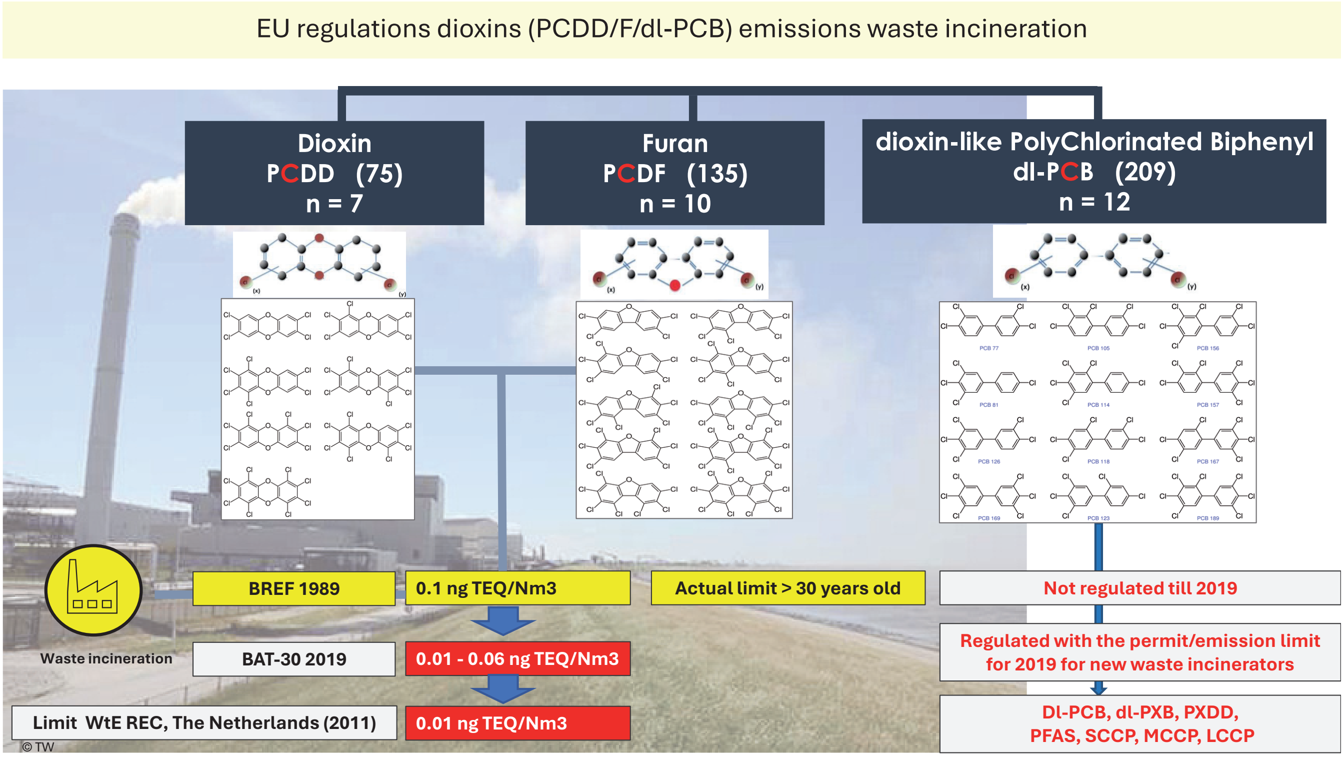
8. Temporal monitoring – analyses of technical data for flue gasses

These newly built waste incineration plants in Zubieta and Beringen have semi-continuous measurement regimen for dioxin and furan (PCCD/F) emissions through long-term flue gas sampling. In principle, this system should be able to provide adequate temporal monitoring, but it appears to be prone to malfunction-



Credit: ToxicoWatch; used with permission.

Figure 12: Example of interruptions in the semicontinuous sampling of flue gases of a waste incinerator.



Credit: ToxicoWatch; used with permission.

Figure 13: EU regulations: permit thresholds for dioxins emission in flue gasses from waste incinerators.

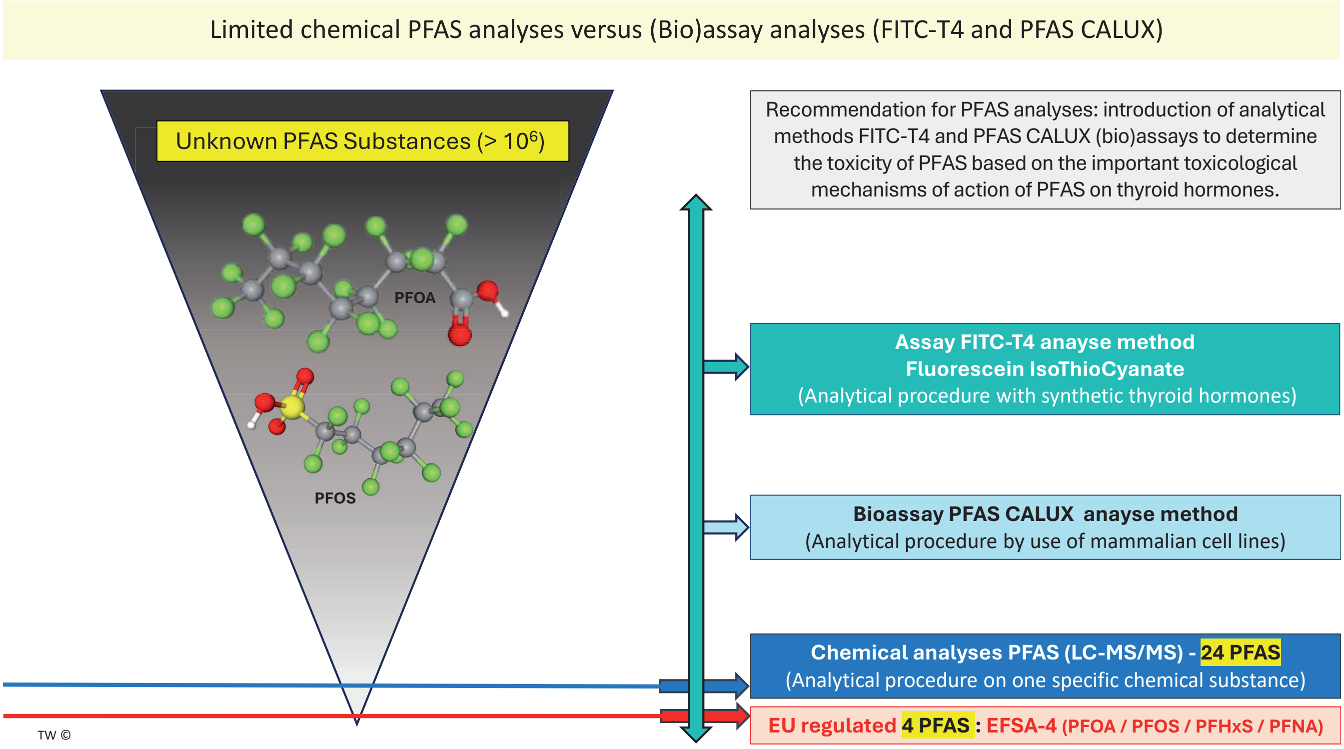
ing exactly at the very moments when measurements are mostly needed. Monitoring is brought to a halt when flue gas flow drops below a given velocity, similarly for temperature, and/or oxygen levels. This unfortunately results in that sampling stops exactly *when there is an enhanced likelihood* for production of elevated levels of toxic substances such as dioxins, PFAS, and PAH – rather the opposite of what is required. Figure 12 shows an example of a similar situation in Paris, France where TW has performed technical research on the semi-continuous minute data of the flue gasses for two years.

9. Temporal monitoring rationale – consequences

Situations deviating from normal operation conditions during waste incineration are referred to as 'Other Than Normal Operating Conditions' (OTNOC). New EU rules specifically address this issue, acknowledging that increased dioxin (PCDD/F/dl-PCB) emissions likely can occur during these events. But the implementation of this new monitoring regime is proving difficult because measuring dioxins during a calamity such as a shutdown or start-up is technologically challenging.
In many countries, there has been hardly any modification of the maximum limit of emissions of dioxins. For example, this limit has since 1989 stood at 0.1 ng TEQ/Nm^3. It is only now that some countries are adjusting the limit down to 0.04 - 0.06 ng TEQ/Nmn^3 for waste incinerators, according to the Best Available Techniques BAT-30 (Neuwahl, et al., 2019). However, there is still a limited regulatory policy based on analysis only of 17 chlorinated dioxins and not for chlorinated dioxin-like PCBs (regulated with an emissions permit of 2019), nor for brominated or mixed halogenated dioxin - and there is no monitoring of PFAS emissions, Figure 13. From a toxicological point of view this is decidedly *worrying*.

10. PFAS and combustion-related emissions

TW was one of the first entities to find and measure PFAS (2016-2017) in flue gas data from the latest state-of-the-art WtE waste incinerator REC/Harlingen, in the Netherlands. In the following years, TW has conducted analyses for PFAS in *eggs*, *mosses (Bryophytes)*, *pine needles (Picea abies, Pinus sylvestris)*, soil, sediment, water, and *wildlife*. The findings of toxic compounds such as dioxins, PFAS and heavy metals, is a clear call-to-action for the responsible authorities to ensure, by (semi-) continuous monitoring of the flue gases, public health safety for the populations living in the surrounding areas.



Recommendation for PFAS analyses: introduction of analytical methods FITC-T4 and PFAS CALUX (bio)assays to determine the toxicity of PFAS based on the important toxicological mechanisms of action of PFAS on thyroid hormones.

Figure 14: Limited chemical PFAS analyses of fluorinated substances versus (Bio)assay analyses (FITC-T4 and PFAS CALUX).

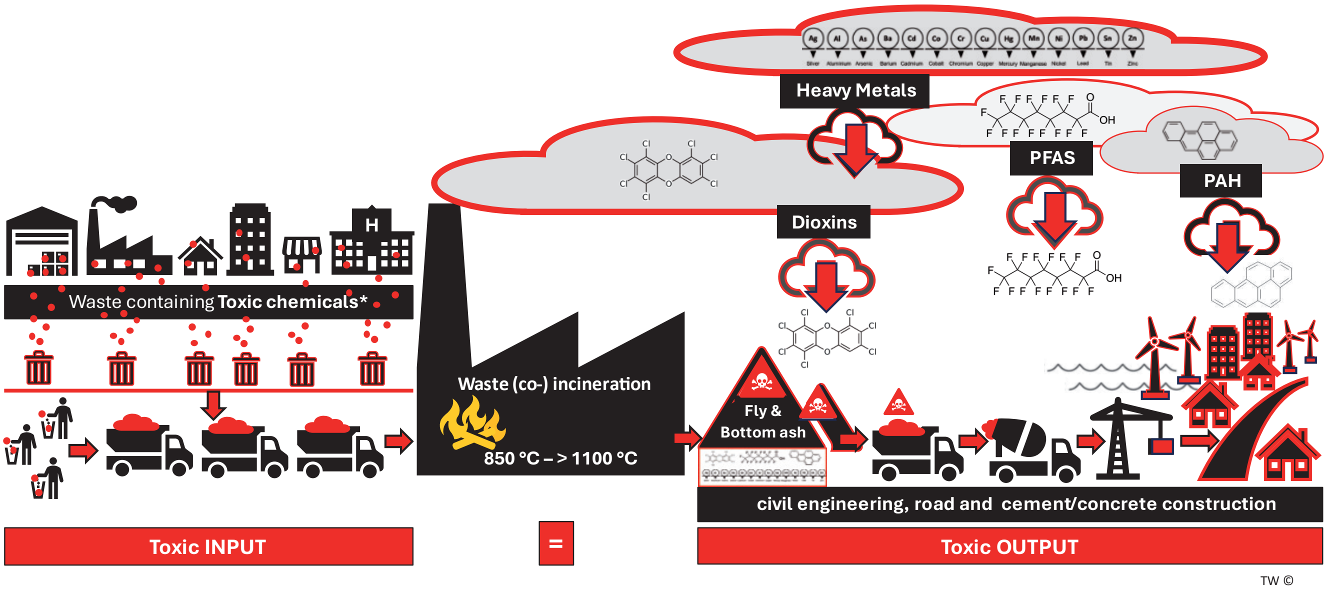
Credit: ToxicoWatch; used with permission.

For broad screening of toxic fluorinated substances TW applies chemical PFAS analyses on 24 fluorinated compounds by use of (bio)assay PFAS CALUX and FTIC-T4, Figure 14. Many PFAS are possible thyroid hormone system disrupting compounds, because they have the capacity a.o. to inhibit the TH thyroxine (T4) from binding to its transport protein transthyretin (de Schepper, et al., 2023).

Approximately 68 million tonnes of municipal solid waste were incinerated in 2017 by all 27 countries in the EU, which generated about 15 million tonnes of municipal solid waste incineration bottom ash (MSWI BA). According to EU's new "Green deal" strategy, these solid wastes are intended to be a valuable resource as secondary raw materials. Thus, after separation of metals, the remaining mineral fraction is mostly reused as unbound aggregates for construction of road base layers and used in civil concrete construction works. However, "the pollution is passed on to future generations," according to the Human Environment and Transport Inspectorate (2019). A full review of bottom ash is given in the report of Arkenbout and Bouman (2025), Figure 15.

TW biomonitoring research employs chemical analyses of 16 different PAH substances, and if needed (for example triggered by high analytical results) these are extended with PAH bioassay analyses (PAH CALUX), giving a broader scope of the effect of PAH substances.

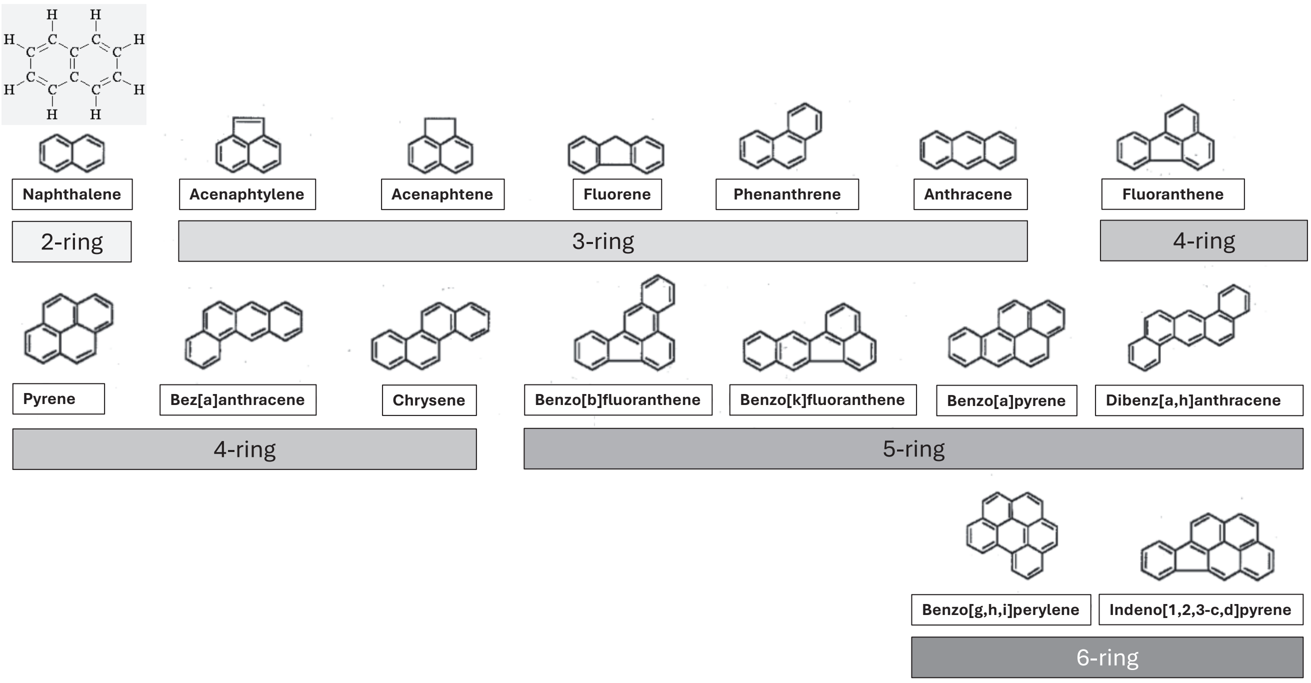
It is important to note that this group is quite extensive and that a significant proportion of the substances cannot be analysed via conventional chemical methods. Two and three-ring PAH are emitted by petrogenic (petroleum and by products) emissions, like car exhaust gases. Four-ring PAH is pyrogenic source related, like natural forest fires and (natural) burning of biomass. PAH that contains a five or a six-ring are Pyrogenic related, meaning from industrial combustion high temperatures (850-1600 C degrees). An overview of the 16 PAH congeners of chemical analysis is presented in Fig. 16.



* Input toxic chemicals in waste: household / consumer / food / industrial waste / retail waste / hospital waste / medical products: have a risk of containing i.e. chlorinated, brominated, fluorinated compounds, Dioxins, PCBs, PFAS , Heavy Metals

Figure 15: Pathways of PFAS, Substances of Very High Concern (SVHC) from waste content into toxic emissions and residues.

Credit: ToxicoWatch; used with permission.



Credit: ToxicoWatch; used with permission.

Figure 16: Congeners (16) of Polycyclic Aromatic Hydrocarbons (PAH) in chemical analyses.

11. Biomonitoring the surrounding environment of the cement kiln, Turňa nad Bodvou, Slovakia

In 2024, a TW biomonitoring program was started concerning possible emissions from a cement kiln in the region of Turňa nad Bodvou in Slovakia, which is fuelled a.o. by co-incineration of PCB oil, old used car tyres and limestone from mining operations. An extensive program was initiated based on samples of backyard chicken eggs/eggshells, wildlife meat from deer, Carp fish (*Cyprinus carpio*), wildlife bird eggshells from Heron (*Ardea*), mosses (*Bryophytes*), pine needles (*Picea abies*), water from natural water stream and wells, sediment from natural water streams and wells; soil was also collected and analysed in accredited labs in the Netherlands.

Substances like dioxins, PFAS, PAHs, and heavy metals are extremely toxic even at very low concentrations and are currently only minimally monitored in the environment of the cement kiln. The population in the vicinity of these facilities lacks transparent emission information from this potential source of pollution. Raw analytical information, preferentially with high resolution, will allow the powerful variographic characterisation well known from the TOS regime (Esbensen 2025). TW started research on the cement kiln in 2023, while the government began environmental biomonitering activities for the first time in 2024.

TW began with analysing fourteen heavy metals (Ag, Al, As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sn and Zn) in soil and found a children's playground in Dvorníky-Včeláre seriously contaminated with lead (Pb) 110 mg/kg and Arsenic (As) 48 mg/kg; the playground is situated at the short distance of 600 meters from the cement kiln. If/when a child ingests soil from this playground (adsorbed on skin, hand or food, or on food), there is a very likely risk it will exceed the tolerable daily intake of lead and arsenic. The risks of both metals are known to cause adverse neurodevelopmental effects, e.g., reduction of cognition and reasoning abilities (Sprong et al., 2023; Swartjes et al., 2017). Further research is *urgently* needed, as these high levels of heavy metals send a strong warning.

12. Heavy metals in mosses (*Bryophytes*)

As part of the same research and monitoring project, TW has also carried out analysis for the same set of 14 heavy metals (HM) in eggshells, pine needles (*Picea abies*) and mosses (*Bryophytes*).

FACTBOX - Sampling mosses (*Bryophytes*) for biomonitoring

Many organisms in the plant kingdom are commonly called *mosses*, even if belonging to different groups of organisms, like *lichens* (symbionts of algae and fungi) or ‘Club moss’, ‘Spanish moss’ (which belongs to the group of vascular plants), and even ‘Irish moss’, but the latter species belongs to the group of algae. In TW biomonitoring research, only mosses from the phylum *Bryophyta*, specifically from the Class *Bryidae*, which contains most moss species in the world (> 9500), are used and analysed to monitor the aerial load of persistent organic pollutants (POPs).

Credit: ToxicoWatch; used with permission.

Figure 17: Sampling mosses (*Bryophytes*) for biomonitoring, photos showing moss sampling in natural refence areas in Zubieta, Basque Country, Spain and in Paris, Ivry-sur-Seine in France 2024.

Unlike vascular plants, mosses lack specialized vascular tissues such as xylem, conducting cells (uptake water and dissolved minerals from the root system to the rest of the plant, and proving physical support) and phloem, the sieve tube cells (tissue for transport glucoses/energy, located behind the bark tissue), besides true roots, stems, and leaves. This means *bryophytes* rely on direct absorption primarily through their leaflike and stemlike structures, or directly through the cells of their gametophyte body for water and nutrients, and thus, also for POPs.

Their surfaces are in direct contact with the environment, allowing them to absorb substances from the ambient air and water. This characteristic makes mosses effective bioindicators for monitoring environmental pollution, as they constantly accumulate pollutants from their surrounding habitat.

The uptake of persistent organic pollutants (POPs) such as dioxins, polycyclic aromatic hydrocarbons (PAHs), per- and polyfluoroalkyl substances (PFAS) and heavy metals can differ between *bryophyte* species. Several factors contribute to these differences:

1. **Surface area and morphology**: Different *Bryophyte/Bryidae* species have varying surface areas and structural features, which influence the extent of pollutant absorption. Species with a larger surface area can absorb more pollutants.

2. **Habitat Preference**: *Bryophytes* that grow in different environments may be exposed to varying levels of pollutants. For example, species that thrive in urban or industrial areas will encounter higher ambient concentrations of certain pollutants compared to those in more pristine natural environments.

3. **Physiological and biochemical Differences**: Different species may have varying capacities for binding, sequestering, or metabolizing pollutants. These physiological and biochemical differences can affect how pollutants are absorbed, translocated, or stored within the plant.

4. **Cuticle development**: The cuticle is a fatty/wax 'skin' layer of plant leaves. The waxy cuticle and stomata (pores on the leaf surface for gas exchange) are of importance for transport of these xenobiotics and makes these organisms good biomarkers (Matos et al., 2022). While *bryophytes* generally have a poorly developed cuticle, the degree of cuticle development can vary among species, potentially influencing pollutant uptake. The lipid content of the cuticle, which may divers between species, is important for xenobiotic transport.

5. **Water retention capacity**: Species with higher water retention capacities might hold pollutants longer, affecting their uptake and accumulation.

Overall, differences in uptake among *bryophytes*/mosses species must be considered when used as bio-indicators for monitoring environmental POP pollution, as they may also reflect the levels and types of other aerial compounds present in their habitats. Their use for biomonitoring is dependent upon *competent identification* and the use of *composite sampling* involves balanced material increments across year-classes: only on this basis can analytical levels between polluted and reference areas be reliably compared. These challenging aspects of analyte quantification are the object of focused R&D for ToxicoWatch, to be reported in due time.

When the moss samples collected in the surrounding area of the cement kiln are compared with *reference samples* collected at locations in the Slovak Karst National Parc (SKNP) 20 km away, strong local elevations are revealed. At some locations, a factor of 10 more heavy metal loads is observed. If the content of heavy metals in mosses is compared with EU regulations, or to recommended national limits, there is a warning signal for Al, As, Co, Cu, Ni, Pb and Sn. The living environment in this area is under strong pressure and may pose health risks for the local population if/when consuming homegrown vegetables and fruit. These results are grounds for an urgent call for a more intensive and comprehensive monitoring of heavy metals in the environment of the cement kiln industry and other (co-) waste combustion-related industries.

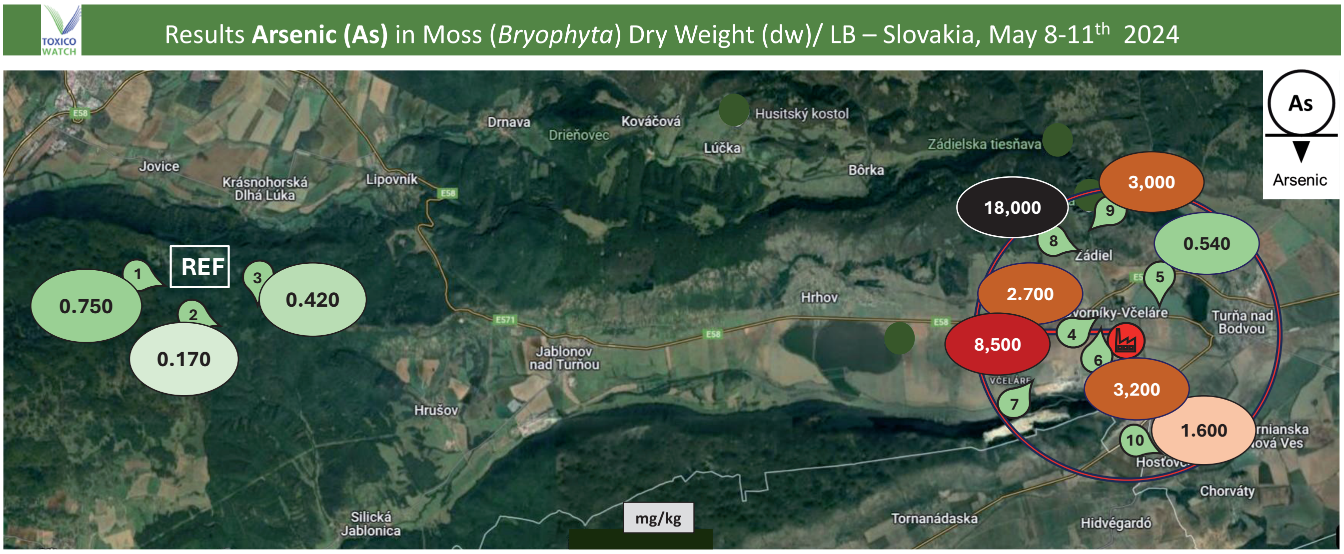
The key issue is whether the observed increased heavy metal concentrations are residues of (historical) agricultural pesticide use or the result of emissions from the cement kiln? To make a judgement about the source of this pollution, uncorrected (semi-) continuous minute-by-minute data from the cement kiln control room is required, including data/measurements during calamities. Monthly monitoring of several hours will be required, but most industry still operates on a measurement regime of only a few hours every six months, announced in advance at that. Given the concentrations of POPs that are detected in the environment, these measurements should be extended with periodic independent biomonitoring to protect the environment and people's health.

Presented below are further examples of TW biomonitoring of heavy metal loads in mosses collected in the vicinity of the cement kiln in the region of Turňa-nad-Bodvou, Slovakia compared with samples in the nature reserve of the Slovak Karst National Park (SKNP) collected using the same field procedures. Concentrations as much as 40 times higher than in the reference samples are observed.

There is a special caution regarding the level of arsenic (As), which in some places is as much as 360 times higher than the safe limit value for arsenic in vegetables to be allowed for consumption, Fig. 18.

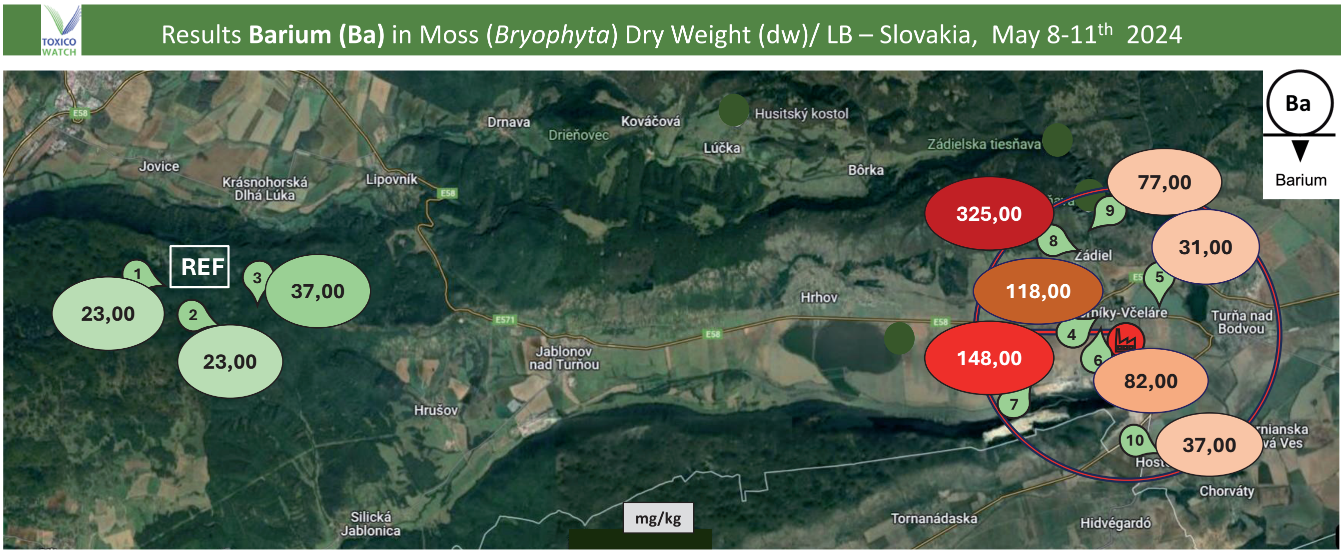
12.1 Barium (Ba)

It is striking that several heavy metals are not measured by default in cement kiln emissions, for instance, Barium (Ba) even though this metal is used in the cement formulation. Cement containing barium (Ba) is used as a binder that resists various types of radiation. Barium (Ba) is extensively used in manufactured materials, including tiles, automobile clutch and brake linings, rubber, brick, paint, glass, and other products. Unusually high concentrations of this metal in soils may indicate anthropogenic activity. Additionally, Barium is commonly found in wastes. For Barium, the Dutch Health Organisation, RIVM, use a tolerable daily intake of 0,6 mg/kg body weight/day, following the approach of the US Agency for Toxic Substances and Disease Registry (ATSDR) in its 2005 report on the toxicological profile for barium, based on animal experiments data (Commission Regulation (EU), 2013).



Credit: ToxicoWatch; used with permission.

Figure 18: Analytical results for Arsenic (As) in mosses (*Bryophytes*) in the environment of the cement kiln, Turňa-nad-Bodvou, Slovakia.



Credit: ToxicoWatch; used with permission.

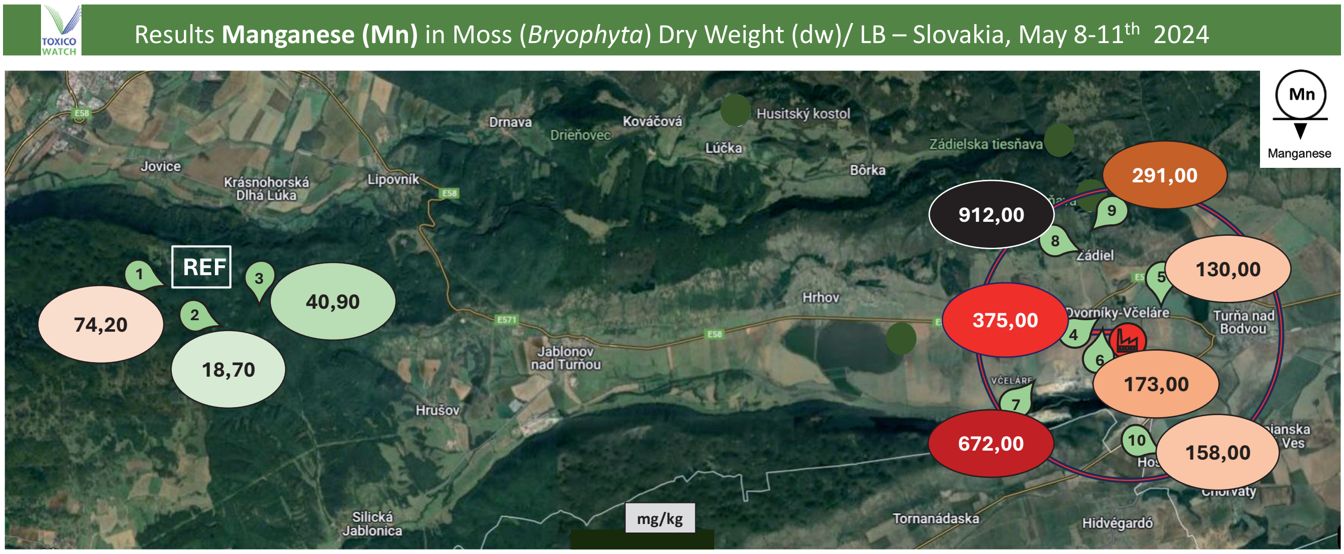
Figure 19: Results Barium (Ba) in mosses (*Bryophytes*) in the environment of the cement kiln, Turňa-nad-Bodvou, Slovakia

The observed Ba levels in mosses in area surrounding the cement kiln in Turňa-nad-Bodvou, Slovakia are presented in Fig.19, locally revealing *very high* levels.

12.2 Manganese (Mn)

Manganese is one of the major trace metals in ordinary Portland cement, which is mainly introduced from alternative fuels and secondary raw feeds during the combustion process of clinker production. Remarkably, no monitoring program is applied for this heavy metal by the cement kiln. Manganese (Mn) emissions and deposition are also related to incinerator processes (Rovira J. et al., 2010).

Long-term exposure to high levels of Manganese can result in serious health effects on the central nervous system such as visual reaction time, hand-eye coordination and hand steadiness. Exposure to higher levels over a long period can result in a syndrome known as *manganism*, which leads to feelings of weakness and lethargy, tremors and psychological disturbances (Kwakye et al., 2015). Figure 20 presents the analytical results for Mn in mosses, with an identical pattern of local *very high* levels as was observed for Ba.



Credit: ToxicoWatch; used with permission.

Figure 20: Results Manganese (Mn) in mosses (*Bryophytes*) in the environment of the cement kiln, Turňa-nad-Bodvou, Slovakia.

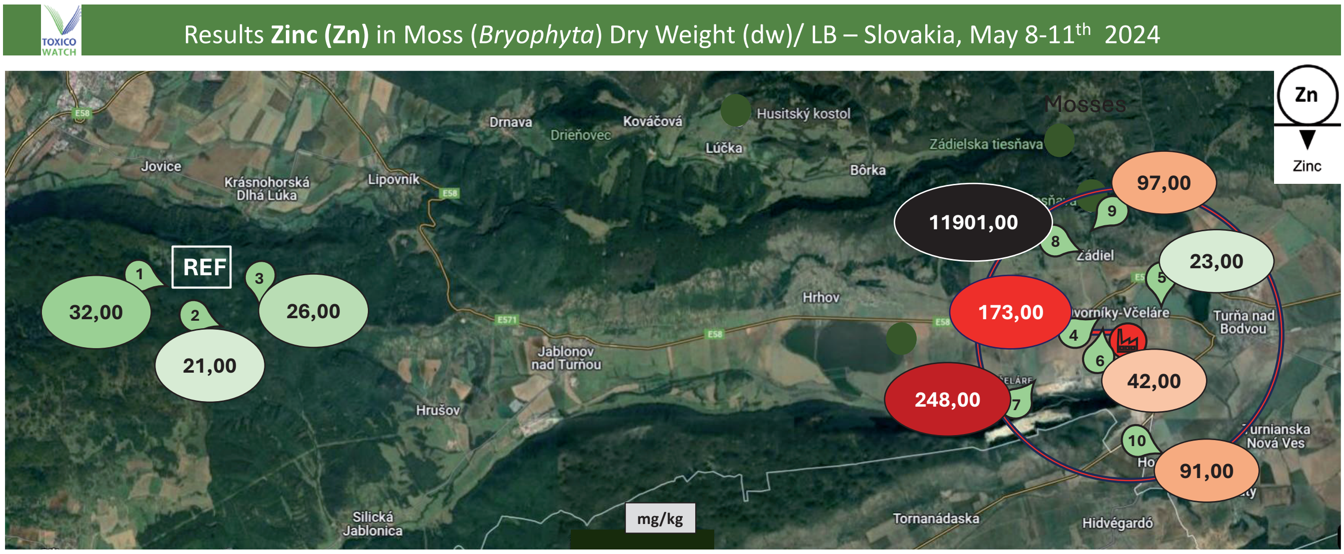
12.3 Lead (Pb)

Lead (Pb) is a naturally occurring element and is one of the longest-established poisons, as emphasised by recent excavations in Pompeii and Herculanum: it is today well-known that many Romans lived in a state of constant lead poisoning due to the widespread use of lead in water piping systems. In addition, it was historically in use in orchards. Lead (Pb) is a highly toxic bio accumulative element, which doesn't degrade easily when metabolized. Rădulescu and Lundgren (2019) found measurable cognitive decline (reduced IQ, academic deficits), especially in children. Lead (Pb) exposure can cause *plumbism*, anaemia, nephropathy, gastrointestinal colic, and degenerative central nervous system symptoms. Neurological symptoms include ataxia, encephalopathy, seizure, swelling of the optic nerve, and disorder of consciousness. The EU regulation for the Maximum Level (ML) of lead (Pb) is set at 0.1 mg/kg wet weight (ww) for fruits and roots, and 0.3 mg/kg ww for leafy greens (EU Commission Regulation, 2023).

All moss samples in the TW Slovak research area exceed the EU maximum limit for lead (Pb) in vegetables, in some locations by more than a factor of 1000! The current consensus is that no level of lead (Pb) exposure should be considered as 'safe'.

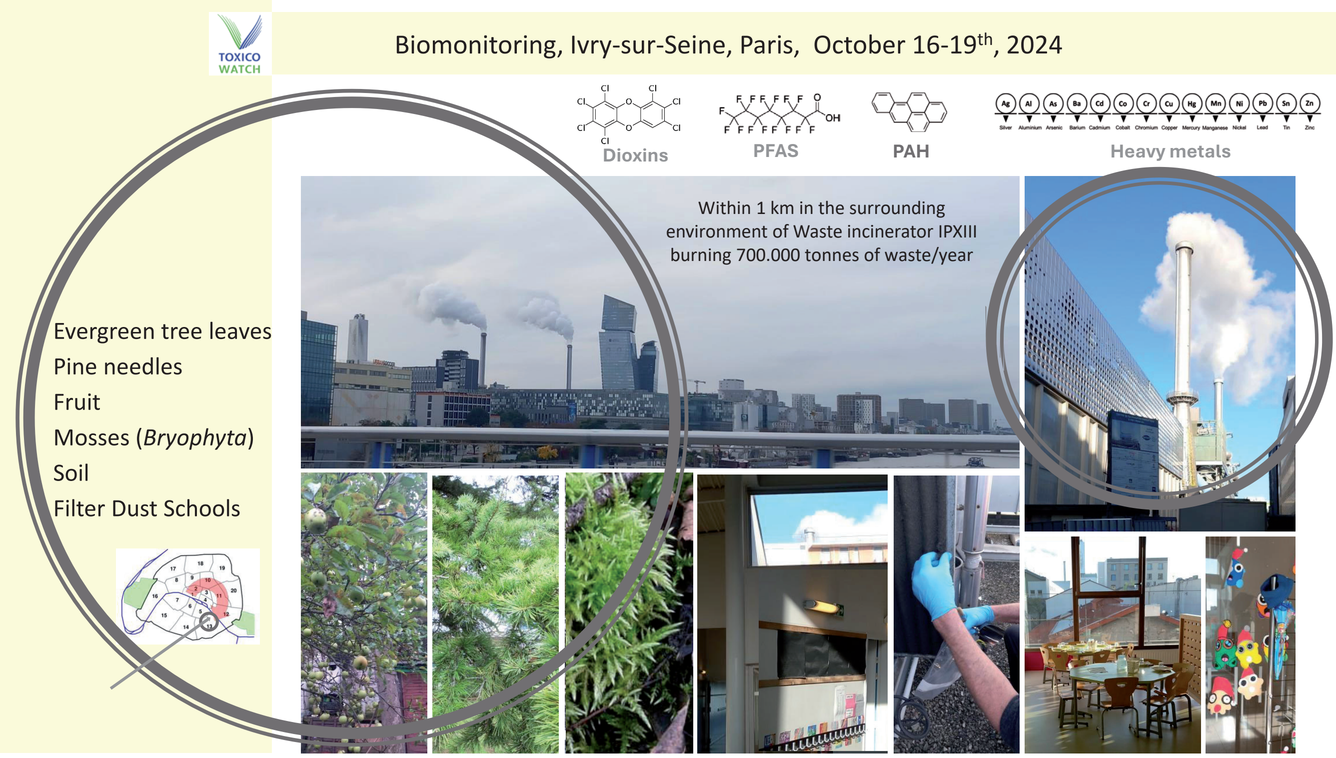
12.4 Zinc (Zn)

Zinc is a heavy metal, which is not monitored by the cement kiln. But zinc is overwhelmingly present in waste streams, according to TW analytical results of water and sediment samples in 2024. A major source of zinc is car tyres. Because cement kiln plants also burn used car tyres, and despite included in the European Green Deal, Zinc will be emitted as a highly volatile metal. Atmospheric emissions of Zinc from anthropogenic sources are an important source which can enter the human body by dispersion, deposition, assimilation by plants and transfer through the food chain, which can result in adverse human health effects. Li et al., (2024) found that excessive exposure to Zn from the ambient air can cause chronic bronchitis, peritonitis, emphysema, asthma and lung cancer. At some locations in *Turňa-nad-Bodvou* TW found extremely high levels of zinc (Zn) in the biomonitoring samples, exceeding the average concentration of zinc (Zn) in vegetables at certain locations by a factor of 10 – 2000 (Fig. 21).



Credit: ToxicoWatch; used with permission.

Figure 21: Zn results in mosses (*Bryophytes*) in the environment of the cement kiln, Turňa-nad-Bodvou, Slovakia.



Credit: ToxicoWatch; used with permission.

Figure 22: TW Biomonitoring research in Paris, Ivry-sur-Seine, 2024-2025.

13. Biomonitoring of POP emissions on primary school filters, Paris

In 2025, TW will conduct biomonitoring research in Paris (dioxins, PFAS, PAH and heavy metals) using dust collected from primary school filters, constructed to filter outside air led into school buildings situated in the surrounding area of the rebuilt waste incinerator Ivry Paris XIII. TW will use vegetation and soil sampling media on the school grounds to compare dust contamination levels from the filters. It is unique that TW has obtained approval from the primary school management to deploy dust filters on the roof of the school building in the vicinity of the waste incinerator. Three years earlier, in 2021, TW started biomonitoring on privately held backyard chickens, mosses and other vegetation in this section of Paris to determine general dioxin contamination levels in the urban region of the urban capital. In addition to analyses of dioxins and PFAS, in 2025, TW's project will also focus on heavy metals in mosses (*Bryophytes*), pine needles (*Picea abies* and *Pinus sylvestris*), and in the soil with the aim of comparing loads as determined from these diverse biomonitoring sampling media with the analytical results from the primary school dust filters. Results will be presented later in 2025 in relevant outreach publications.

14. Perspective

The last 13 years of TW performing biomonitoring research in the surrounding environment of POP emitting industries has clearly demonstrated the need for, and value from, continuing of this kind of studies and monitoring to get a better science-backed understanding of pollution levels in contaminated industrial regions. Use of innovative bioaccumulating sampling media began in 2013 and has provided a challenging R&D focus point ever since. So far, a wide range of sampling media has been tested out, with selected results presented here.

The use of conventional as well as novel sampling media is a highly challenging scientific and technological field in constant development, which is addressed with all available efforts. It is of special interest for the readership of this journal that the representativity of the sampling procedures used/developed must be thoroughly monitored and documented, especially for the innovative sampling media. This is carried out by parallel practical sampling campaigns based on Replication Experiments (RE) and variographic characterisation, well-know within the Theory of Sampling (TOS) (Esbensen, 2024).

However, it must be mentioned that such scientific baseline documentation constitutes quite a load on a Not-for-Profit public organisation running on sponsorships from the public. Lots of voluntary work is still needed and more funding from concerned stakeholders (civil, industrially based and governmental) is very much welcomed.

ZERO WASTE EUROPE BIOMONITORING

This video shows how biomonitoring is becoming a vital tool in the demand for environmental transparency. Learn how you can join this growing movement for change in your own community.

youtu.be/YFQWpDjC2xs

15. ToxicoWatch and 'Zero Waste Europe' support

TW started research on demand of concerned local people and local politic parties in Harlingen, The Netherlands in 2013 by TW's own initiative an independent biomonitoring study on dioxins in backyard chicken eggs in the surrounding environment of the newly built WtE waste incinerator REC (2011). The high documented level of dioxins in these eggs resulted in national attention with several documentaries on national Dutch TV and counter research from the Ministry of Health (VROM). From 2014 till 2019 TW has presented these results at Dioxin conferences and other relevant toxicological conferences and symposia (SETAC, INEF and BDS) about the NL research findings as well of TW biomonitoring in other European countries on POP in relation to emissions of waste incineration. TW attended, based on its research, the Basel Rotterdam Stockholm conventions (BRS COPs 2017 & 2019). Since 2021 *Zero Waste Europe* in Brussels has supported TW financially regarding multi-year biomonitoring research projects and on POPs in in surrounding areas of (co-) waste incineration in several European countries (see Fig. 23 and video on the left).

Additionally, Toxicowatch is engaged in a continuing educational outreach activity bridging between local populations, industry and governments (Fig. 24).


ToxicoWatch 12 years of Biomonitoring Research on POPs, 2013-2025

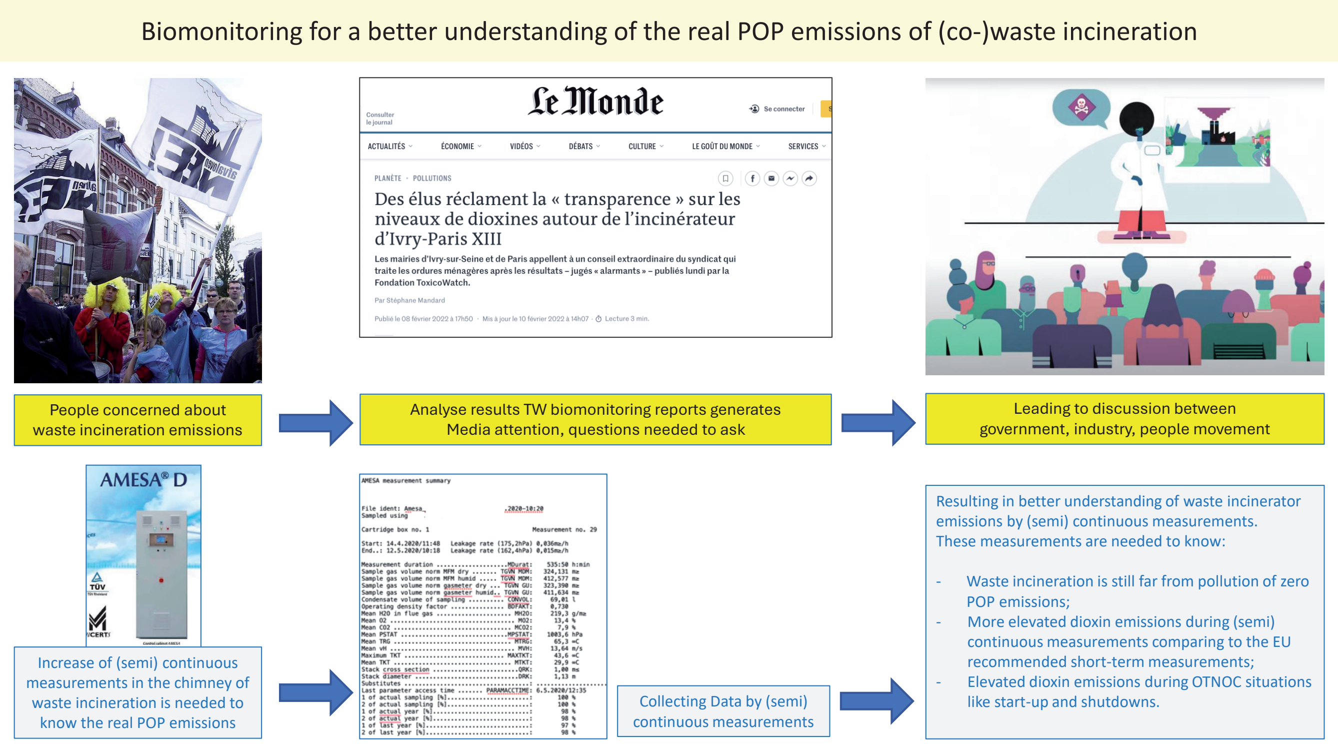
Country		City / Region	(Co-) Waste Incineration	Year start of production	ToxicoWatch Biomonitoring Research
					Zero Waste Europe
Basque Country/Spain	EUS	Zubieta	WtE Zubieta	2020	**2019** - 2023 (2025)
Slovakia	SK	Košice	Cement kiln Turňa nad Bodvou	1973 (1992, 2011)	2023 - 2024 (2025)
The Netherlands	NL	Harlingen	WtE REC	2011	**2013** - 2023 (2025)
Belgium	BE	Beringen	WtE Bionerga	2020	**2019 - 2022** (2024/25)
France	FR	Paris	Ivry-Paris XIII	1969 (1995, 2005)	**2021 - 2023** (2024/25)
Spain	ES	Madrid	Valdemingómez	1996	2021 - 2022
Czech Republic	CZ	Pilsen	WtE ZEVO Plzeň	2020	2021 - 2022
Lithuania	LT	Kaunas	WtE UAB Kauno	2020	2021 - 2022

www.zerowasteeurope.eu/project/the-true-toxic-toll

www.toxicowatch.org

Credit: ToxicoWatch; used with permission.

Figure 23: TOXICOWATCH biomonitoring research outreach 2013-2025 (www.toxicowatch.org)



Biomonitoring for a better understanding of the real POP emissions of (co-)waste incineration

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PLANÈTE · POLLUTIONS

Des élus réclament la « transparence » sur les niveaux de dioxines autour de l'incinérateur d'Ivry-Paris XIII

Les mairies d'Ivry-sur-Seine et de Paris appellent à un conseil extraordinaire du syndicat qui traite les ordures ménagères après les résultats – jugés « alarmants » – publiés lundi par la Fondation ToxicoWatch.

Par Stéphane Mandard

Publié le 08 février 2022 à 17h50 · Mis à jour le 10 février 2022 à 14h07 · Lecture 3 min.

People concerned about waste incineration emissions

Analyse results TW biomonitoring reports generates Media attention, questions needed to ask

Leading to discussion between government, industry, people movement

Increase of (semi) continuous measurements in the chimney of waste incineration is needed to know the real POP emissions

```
AMESA measurement summary



File ident: Amesa_                        .2020-10:20
Sampled using

Cartridge box no. 1                           Measurement no. 29

Start: 14.4.2020/11:48   Leakage rate (175,2hPa) 0,036m³/h
End..: 12.5.2020/10:18   Leakage rate (162,4hPa) 0,015m³/h

Measurement duration .....................MDurat:    535:50 h:min
Sample gas volume norm MFM dry ....... TGVN MDM:   324,131 m³
Sample gas volume norm MFM humid ..... TGVN MDM:   412,577 m³
Sample gas volume norm gasmeter dry ... TGVN GU:   323,390 m³
Sample gas volume norm gasmeter humid.. TGVN GU:   411,634 m³
Condensate volume of sampling .......... CONVOL:     69,01 l
Operating density factor ............... BDFAKT:     0,730
Mean H2O in flue gas ..................... MH2O:     219,3 g/m³
Mean O2 ................................... MO2:      13,4 %
Mean CO2 .................................. MCO2:      7,9 %
Mean PSTAT ..............................MPSTAT:    1003,6 hPa
Mean TRG ................................. MTRG:      65,3 °C
Mean vH ................................... MVH:     13,64 m/s
Maximum TKT ............................ MAXTKT:      43,6 °C
Mean TKT ................................. MTKT:      29,9 °C
Stack cross section .......................QRK:      1,00 m²
Stack diameter ............................DRK:      1,13 m
Substitutes ..................................: ..................
Last parameter access time ....... PARAMACCTIME: 6.5.2020/12:35
1 of actual sampling [%].......................:        100 %
2 of actual sampling [%].......................:        100 %
1 of actual year [%]...........................:         98 %
2 of actual year [%]...........................:         98 %
1 of last year [%].............................:         97 %
2 of last year [%].............................:         98 %
```

Collecting Data by (semi) continuous measurements

Resulting in better understanding of waste incinerator emissions by (semi) continuous measurements.
These measurements are needed to know:

- Waste incineration is still far from pollution of zero POP emissions;
- More elevated dioxin emissions during (semi) continuous measurements comparing to the EU recommended short-term measurements;
- Elevated dioxin emissions during OTNOC situations like start-up and shutdowns.

Credit: ToxicoWatch; used with permission.

Figure 24: Biomonitoring for a better understanding of the real POP emissions of (co-) waste incineration.

16. Conclusions

It can be concluded that biomonitoring is essential as a tool for monitoring the *real* deposition of industrial emissions of hazardous POP substances in the surrounding (human) environment. An important result of TW's work and research is that local communities become involved and are actively participating in the practical realisation of highly relevant research projects. With this approach, local communities feel listened to, and experience in practice that action is taken to focus their serious concerns through citizen-participation, scientific research, and communication with governments and other relevant organisations. In this way, TW acts as a bridge between local communities, industry, and government.

Authorities must prioritise elimination of harmful POP industrial emissions, on behalf of a reasonable and fair precautionary principle, to give human and environmental health priority over industry management focused on economic profit-oriented considerations. This master principle should guide every effort to address the significant environmental and public health concerns illustrated. If unmitigated these concerns will even harm businesses and and national economies as well.

It is of critical importance to maximise *dissemination* of the results of relevant biomonitoring studies as well as encourage further citizen-driven counter activities against harmful industrial emissions. Interested parties and stakeholders are referred to TOXICOWATCH' homepage: www.toxicowatch.org

TOXICOWATCH is grateful for the opportunity to present some of its R&D work to the international sampling community.

LEARN MORE

- **zerowasteeurope.eu/project/the-true-toxic-toll**
- **toxicowatch.org**

References

Arkenbout A., Bouman, K.J.A.M. (2025). 'Saxon Pit', Incineration Bottom Ash (IBA) & Incineration Bottom Ash Aggregate (IBAA), Whittlesey, Cambridgeshire, United Kingdom, ToxicoWatch, March

Arkenbout, A. & Esbensen K.H. (2017). Biomonitoring and source tracking of dioxins in the Netherlands, In *Proceedings of the Eighth World Conference on Sampling and Blending (WCSB8)*, 9–11 May, Perth, WA, The Australasian Institute of Mining and Metallurgy (AUSIMM), Victoria, AUS., pp.117-124

Arkenbout, A., Olie K. & Esbensen K.H., (2018). Emission regimes of POPs of a Dutch incinerator: regulated, measured and hidden issues, *Organohalogen Compounds, 80*, pp.413-416.

Commission Regulation (EU) Report (2013). No. 681, 17 July, https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32013R0681

Commission Regulation (EU) Report (2023). No. 915,25 April, https://eur-lex.europa.eu/legal-content/NL/TXT/PDF/?uri=CELEX:32023R0915 (In Dutch).

De Schepper, J., van Oorschot, Y., Jaspers, R.J., Hamers, T., et al. (2023). The contribution of PFAS to thyroid hormone-displacing activity in Dutch waters: A comparison between two in vitro bioassays with chemical analysis. *Environment International, 181*, 108256. https://doi.org/10.1016/j.envint.2023.108256

Dioxin 20XX International Symposium, https://dioxin20xx.org

DS 3077 (2024). *Representative Sampling— Horizontal Standard*, (3rd ed.). Danish Standard Foundation, Nordhavn, Copenhagen, DK. https://webshop.ds.dk/en/standard/M374267/ds-3077-2024

Esbensen, K.H. (2025) *Introduction to the Theory and Practice of Sampling*, Wedel, DE., SIX-Publishing ISBN 978-3-9826493-1-3

Commission Regulation (EU) Report (2013). No 681, 17 July, Amending part III of Annex II to Directive 2009/48/EC of the European Parliament and of the Council on the safety of toys, https://eur-lex.europa.eu/eli/reg/2013/681/oj/eng

Commission Regulation (EU) Report (2023). No. 915, 25 April, *Betreffende maximumgehalten aan bepaalde verontreinigingen in levensmiddelen en tot intrekking van Verordening (EG) nr. 1881/2006* https://eur-lex.europa.eu/legal-content/NL/TXT/PDF/?uri=CELEX:32023R0915

Hoogenboom, R.L.A.P., Ten Dam, G., van Bruggen, M., Jeurissen,S.M.F., et al. (2016). Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and biphenyls (PCBs) in home-produced eggs, *Chemosphere 150*, pp.311-319, May. https://doi.org/10.1016/j.chemosphere.2016.02.034

Human Environment & Transport Inspectorate (Inspectie Leefomgeving en Transport, ILT) (2019). Signal reporting, Analysis of risks in the bottom ash chain/Signaalrapportage, Analyse risico's in de keten van bodemas, https://www.ilent.nl/documenten/leefomgeving-en-wonen/bodem/bodemtoezicht/zienswijzen/analyse-risicos-in-de-keten-van-bodemas

Jovan, S., Jacobson, E., Unrine, J.M. *et al.* (2024). Putting biomonitors to work: Native moss as a screening tool for solid waste incineration. *Environ Monit Assess 196*, 1177. https://doi.org/10.1007/s10661-024-13354-y

Kwakye G.F., Paoliello M.M.B., Mukhopadhyay, S., Bowman, A.B. & Aschner, M. (2015). Manganese-induced parkinsonism and Parkinson's disease: Shared and distinguishable features. *Int J Environ ResPublic Health 12*(7), pp. 7519–7540. https:// doi.org/10.3390/ijerph120707519

Li, J., Li, X., Wang, Y., Meng, L., & Cui, W. (2024). Zinc: a potential star for regulating peritoneal fibrosis. *Frontiers in Pharmacology*, 15. https://doi.org/10.3389/fphar.2024.1436864

Matos, T.M., Cruz, R., Peralta D.F., Melo-de-Pinna, G.F.A. & Santos, D.Y.A.C. (2022). Cuticle structure and chemical composition of waxes in Phaeoceros laevis (L.) Prosk (Notothyladaceae, Anthocerotophyta. Front. *Plant Sci. 13*:785812. https://doi.org/10.3389/fpls.2022.785812

Musilová, J., Franková, H., Lidiková, J. et al. (2022). Impact of old environmental burden in the Spiš region (Slovakia) on soil and home-grown vegetable contamination, and health effects of heavy metals. *Sci Rep* 12,(1).,16371. https://doi.org/10.1038/s41598-022-20847-8

Neuwahl F., Cusano, G., Benavides, J.G., Holbrook, S & Rodier, S. (2019). *Best Available Techniques (BAT) Reference Document for Waste Incineration Industrial Emissions Directive 2010/75EU, Integrated Pollution Prevention and Control, EUR 29971 EN.* https://eippcb.jrc.ec.europa.eu/sites/default/files/2020-01/JRC118637_WI_Bref_2019_published_0.pdf

Qarri, F. Lazo P, Allajbeu S, Bekteshi L, Kane S, Stafilov T. (2019). The Evaluation of Air Quality in Albania by Moss Biomonitoring and Metals Atmospheric Deposition. *Arch Environ Contam Toxicol May* 76, pp. 554–571. https://doi.org/10.1007/s00244-019-00608-x

Rădulescu, A. & Lundgren, S. (2019). A pharmacokinetic model of lead absorption and calcium competitive dynamics. *Sci Rep* 9, 14225. https://doi.org/10.1038/

Sprong, C., Te Biesebeek, J.D., Chatterjee, M., Wolterink, G., van den Brand, A., et al. (2023). A case study of neurodevelopmental risks from combined exposures to lead, methyl-mercury, inorganic arsenic, polychlorinated biphenyls, polybrominated diphenyl ethers and fluoride. *Int J Hyg Environ Health*, Jun;251:114167. https://doi.org/10.1016/j.ijheh.2023.114167.

Swartjes, F.A., et al. (2017). Gezondheidsrisico's ten gevolge van arseen in bodem en grondwater in Apeldoorn, RIVM Rapport 2017-0198 https://eur-lex.europa.eu/legal-content/NL/TXT/PDF/?uri=CELEX:32023R0915

Zero Waste Europe (2025) Brussels, Belgium. https://zerowasteeurope.eu/#updates

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Sampling for Glaciological “Erratic Rock” Provenance: The Brilliance of Danish Geologist Arne Noe Nygaard

By Kim H. Esbensen[1]

DOI: 10.62178/sst.003.003

ABSTRACT

This article showcases the extraordinarily versatile Replication Experiment (RE). Although presented and illustrated before within the professional sampling community, there are still many cases showing inspiring, didactic applications allowing a broader view on the types of “analysis” associated with sampling. Although so-called “economic geological processes” are of key importance within the traditional field(s) of sampling (TOS), i.e. mineralisations, ore exploration and mining, minerals processing, the author and editor, here drags the reader into a realm very rarely visited in the sampling realm—academic geology. The present case could just as well have been termed “Danish medieval churches meet inspiring geologic icon inventing the RE independently of the TOS”.

1. A most unusual sampling setting

The present exposé is based on what turned out to be Noe-Nygaard’s last book publication, titled *Larvikitter i Kvaderstenskirke* (DGU Publ. 1991) ISBN 87-88640-74-4 [Larvikites in hewn stone churches].

Barely of book size (only 32 pages), it tells a fascinating geological detective story about the provenance of wall rocks in Danish medieval stone churches in northern and western Jutland. As the name implies, this type of church is built by square hewn rocks of local origin from the local landscape in medieval times. But their ultimate origin is much older—and this is the red line of this article.

ARNE NOE-NYGAARD, DANISH GEOLOGIST (1908-1991)

Noe-Nygaard was a Nestor in Danish and Scandinavian geology through a long and very productive academic career. He was a professor for 40 years, also widely involved in popularising geology and was intimately involved in the founding of The Geological Survey of Greenland (GGU, now GEUS). His biography in Wikipedia is unfortunately only in Danish, but visit it anyway—lots of geology is communicated in pictures, images and maps, and his extensive oeuvre is liberally written in English and German, scientifically spanning from the Pre-Cambrium era in Greenland and Denmark to the present (the Quaternary) with a focus on volcanology in Iceland, Greenland and the Faroe Islands, as well as many other topics, one of which is presented in the present article.

Credit: Preben Nielsen; reproduced with permission from GEUS.

Figure 1: Arne Noe-Nygaard at his desk at the Geological Museum, Copenhagen at the time of his retirement from a 40-year position as professor in dynamic geology at the University of Copenhagen.

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[1] KHE Consulting, Copenhagen, Denmark

Arne Noe-Nygaard

Larvikiter i kvaderstenskirker

DGU Miljøministeriet Danmarks Geologiske Undersøgelse

Figure 2: Front page of Larvikites in Hewn Stone Churches published posthumously in 1991. Arne Noe-Nygaard died on 4 June 1991, but managed to edit the first proof of the book just before passing. An active geologist and scientist right up until the end.

The Romanesque hewn rock churches in Jutland were constructed in the period 1100-1200. There are still some 700 of them in a reasonably wellpreserved state. In fact, this type of church is rather unique for the northern and western parts of Jutland, hardly found anywhere else in the world.[1,2] It is the professional historical view that the source for the rocks used for the original church building is local, i.e. they represent the surrounding landscape from where they were transported as short distances as possible before being hewn, probably at the church site. It is easy to compensate for later alterations and additions regarding improvements and modifications often with a distinct later architectural style, e.g., as seen in Figures 2 and 3 (enlargement of windows, lead roofing and addition of a bell tower). Compensating for this, the geologist Noe-Nygaard shared the belief that most of the original church walls in northern and western Jutland represent a wellpreserved sample of the local rocks found on the surface at the time of building.

Figure 3: "Asp Kirke", Jutland, typical medieval Romanesque church illustrating the diverse assembly of hewn rock types. Note later impro vement (enlargement) of windows, later lead roofing and addition of a bell tower.

But why, and how did the medieval landscape come to be strewn with an abundance of boulders and rocks of a size that would suffice well for production of hewn rocks? This is where an underlying relationship between geology and religion has its origin. It is a fascinating story that involves "erratics"...

2. Erratics—composition, origin, glacial transportation

Of the use in everyday language (Meriam-Webster) has the following to say: "Erratic can refer to literal 'wandering'. A missile that deviates from its planned trajectory, and a river with lots of twists and bends is said to have an erratic course. Erratic can also mean 'inconsistent' or 'irregular'. So, a stock market that often changes direction is said to be acting erratically; an erratic heartbeat can be cause for concern; and if your car idles erratically, it may mean that something's wrong with the sparkplug wiring".

In geology, however, this term is distinctly specific. Here erratic is used in one particular sense only, regarding composition, provenance and direction and distance travelled.

Figure 4: Archetypal "erratic". The composition of the conspicuous rock may be similar to the local rock types (short distance travelled only) but, much more often, is of markedly different habitus [travelled over long(er) distances]. CredIt: Daniel Mayer, Creative Commons Attribution- Share Alike 1.0 Generic, Encyclopædia Britannica

Glacial erratics are stones and rocks that were transported by a glacier and were left behind after the glacier melted and retreated. Thus, glacial erratics were formed by erosion ("plucking") as a result from the flowing movement of ice over the local bedrock. Such erratics can range in size from pebbles to large boulders and can have been carried for hundreds of kilometres (800 km is an often quoted maximum). Scientists have a.o. used erratics to help determine ancient glacier movement(s), i.e., directions, distances and other local features. Particularly large erratics end up as marked landscape elements, Figure 4, sometimes associated with much later local historical lore.

Of specific interest to the uninitiated reader, and directly related to the story in this article, is the fact that erratics differ in composition and hence in appearance from the local bedrock upon which they are found; of course, mostly clear to the trained geologic eye. Erratics may be embedded in the finegrained, ground up glacial deposits (called till), or, more often, occur as conspicuously independent special landscape elements on the bare ground surface.

Those transported over long distances generally consist of rock resistant to the shattering and grinding effects of glacial transport. Erratics composed of unusual and distinctive rock types can, by diligent and competent geologists, sometimes be traced to their source of origin and thereby serve as indicators of the direction of glacial movements. Studies making use of such indicator erratics have provided information on the flow paths of the major ice sheets in the ice age(s) of our planet (and indeed also on occasion the location of important mineral deposits). Erratics played an important part in the initial recognition of the most recent ice age(s) and their extent. Originally thought to be transported by gigantic floods or by ice rafting, erratics were first correctly explained in terms of glacial transport by the Swiss-American naturalist and geologist J.L.R. Agassiz in 1840.

Figure 5: J.L.R. Agassiz (1840). Photo: Wikipedia, Public Domain

For more information, see the comprehensive entry on glacial erratics in Wikipedia: https:// en.wikipedia.org/wiki/Glacial_ erratic. In this widely covering entry on glacier-borne erratics, a wealth of examples are described, from Australia, Canada, Estonia, Finland, Germany, Republic of Ireland, Latvia, Lithuania, Poland the United Kingdom and the USA. Curiously, however, there is a distinct lacuna: Norway and Denmark are completely missing, which is a major affront to geologists from these two countries, something to be rectified with a friendly vengeance below!

3. Zooming in...

The reader is now in possession of the necessary subject-matter background for what is to be revealed here below. Here are the telling detective clues:

1) Larvikite is a distinct igneous rock formed by solidifying magma, not as a lava, but as a deep-seated intrusive magmatic body in the Earth's crust. Figure 8 below also shows the source area of known larvikite occurrences in Norway. Igneous rock types are named after the location of the occurrence of the type rock where and when it was first described scientifically.

A few facts of interest:

1) Larvik (https://en.wikipedia.org/wiki/Larvik) is the birth town of the world renowned Norwegian explorer and historian Thor Heyerdal of Kon-Tiki expedition fame.

2) The author of the present column also resided in Larvik for an extended period of time (1980-2000), from which grew a fascination with the particular rock type in question here. The city itself is immensely proud of its world renowned resources of dimension stone, in the form of polished façade rocks, a major export asset.

3) For a thorough description of the geology of larvikite, the comprehensive publication by Heldal et al., (2008) which, although written for professionals, can also be browsed with pleasure by interested parties: https:// www.ngu.no/upload/Publikasjoner/Special%20publication/SP11__02__ Heldal.pdf

2) There are no occurrence of bedrocks of the larvikite type in Denmark—none!

3) But, very many hewn rock churches in the northern and western-most parts of the Jutland peninsula of Denmark contain a definite, identifiable proportion of larvikite rocks in their makeup. There are actually seven recognisable sub-types (varieties) of larvikite involved, which is for the professional geologists to keep track of, but no worries: Noe-Nygaard knew his larvikites!

4) So how come there were decidedly non-native, indeed "erratic" rock types to be found in the walls of medieval churches in Jutland? This was a major mystery at the time when the science of geology was developing in the 19th century. For example, it was suggested that major floods could have been responsible for such marked dislocations, but after the Agassiz breakthrough (1840), a modern understanding was quickly worked out: in earlier times large(r) parts of the continents in the northern hemisphere were covered (one, or several times) by thick sheets of ice, glaciers (really thick ice sheets, e.g., up to 3 km as in the present day inland ice sheet covering Greenland). Erratics were now envisaged as having been transported by the internal flow of ice masses during a specific (or possible recurrent) glacier event(s) during a specific ice age. An important part of this development is concerned with the evidence and the relics left by scouring ice flows interacting with the bedrocks over which it flows, plucking, plucking ...). There is an absolutely overpowering force at work at the bottom of thick ice flows.

5) So, it is no longer a mystery that, for example, larvikite erratics can now be found in Denmark several hundreds of kilometers south of their point of origin; this picture is today well known and accepted. But the details of filling out this broad framework still leaves a lot of complex and highly fascinating questions, answers to which have been worked out by later generations of geologists, and this is where the legacy of Arne Noe-Nygaard's last book comes to the fore. Questions arise, such as which of the three major ice ages that can be recognised in Denmark did this erratic complement of surfacefound stones originate? (There are several other, intricate details involved here, which find their resolution at the end of Noe-Nygaard's account, but these can safely be left to the professional connoisseurs of Quaternary glacial geology). Here we leave such particulars and move fast forward to sampling and analysis in this fascinating context.

6) Noe-Nygaard's book gives readers a highly personal *tour de Jylland* in the form of numerical accounts of the assemblages of hewn rocks to be found in the makeup of the walls of the gamut of Roman churches, broadly constructed in the period 1100-1200. The final result of Noe-Nygaard's investigation is reproduced below as Figure 7, to be further commented upon.

4. In *medias res*: sampling and analysis

So, what kind of sampling was used in this story? And what kind of analysis?

One could perhaps imagine that church rock walls were sampled in the traditional field geological sense with "field samples" brought to the laboratory for petrological, mineralogical and geochemical analysis with a view of identifying the different type of larvikite rocks; thus, their proportions of the complete hewn rock church assembly.

But no, the story is more interesting, and far more personal in a unique sense. In today's sampling and analysis terms as used in science, technology and industry, Noe-Nygaard unknowingly made use of what today is known as a "PAT-approach", although the concept of Process Analytical Technology was not to be established until years later than Noe-Nygaard's first field investigations.

5. A PAT aside[2]

The key aspect of PAT is to perform sampling and analysis in one-andthe- same-operation. Within PAT the focus is nearly always on the many contending analytical modalities competing for attention and each claiming superiority, but there is also an underlying, unfortunately often unrecognised challenge, related to the role of the sampling interface.

The key characteristic of PAT is deployment of sensor technologies (physical probes, chemical sensors, other sensors) intercepting and interacting with a process stream. The key characteristic of PAT is that of performing sampling and analysis simultaneously as one unified process: probes and sensors interact analytically with an often small (sometimes minute) "effective volume" of the flux of matter which represents the support volume from which analytical signals are acquired. This is very often in the form of multi-channel spectroscopic signals, which can be transformed into a predicted chemical or physical measurement, see, for example, the fundamental textbook by Katherine Bakeev, *Process Analytical Technology*,[3] in which chemometrics has made essential contributions by deploying the powerful multivariate calibration approach, e.g., Esbensen & Swarbrick (2018).[4]

Methods and equipment of process sampling are front and centre in the realm of the Theory of Sampling (TOS). The TOS supplies a comprehensive, well-proven framework that derives all principles and implementation demands needed for how to extract representative physical samples from moving lots, i.e., from a conveyor belt or from ducted material streams. PAT aspires to take this situation over to the situation in which the task is how to extract representative sensor signals instead of physical samples.

For "sensor sampling", i.e., PAT, there is no similar foundational framework. Instead, a pronounced practical approach is evident in this realm, in which the question of how to achieve representative sensor signals is not so much related to the design and implementation of an appropriate sampling interface between the sensor and the streaming flux of matter. Rather, a survey of the gamut of sensor interfaces presented in industry and in the literature reveals a credo that appears to be: "Get good quality multivariate spectral data—and chemometrics will do the rest", exclusively relying on multivariate calibration of process sensor signals (multi-channel analytical instruments). There is a tacit misunderstanding that the admittedly powerful chemometric data modelling is able to take on and correct for any kind of sensor signal uncertainty—including "sampling errors". However, this leaves analytical representativity the victim of imperfect under signals, which can be transformed into a predicted chemical or physical measurement, see, for example, the fundamental textbook by Katherine Bakeev, *Process Analytical Technology*,[3] in which chemometrics has made essential contributions by deploying the powerful multivariate calibration approach, e.g., Esbensen & Swarbrick.[4] Methods and equipment of process sampling are front and centre in the realm of the Theory of Sampling (TOS). The TOS supplies a comprehensive, well-proven framework that derives all principles and implementation demands needed for how to extract representative physical samples from moving lots, i.e., from a conveyor belt or from ducted material streams. PAT aspires to take this situation over to the situation in which the task is how to extract representative sensor signals instead of physical samples. For "sensor sampling", i.e., PAT, there is no similar foundational framework. Instead, a pronounced practical approach is evident in this realm, in which the question of how to achieve representative sensor signals is not so much related to the design and implementation of an appropriate sampling interface between the sensor and the streaming flux of matter. Rather, a survey of the gamut of sensor interfaces presented in industry and in the literature reveals a credo that appears to be: "Get good quality multivariate spectral data—and chemometrics will do the rest", exclusively relying on multivariate calibration of process sensor signals (multi-channel analytical instruments). There is a tacit misunderstanding that the admittedly powerful chemometric data modelling is able to take on and correct for any kind of sensor signal uncertainty—including "sampling errors". However, this leaves analytical representativity the victim of imperfect understanding of the nature of data analytical errors (ε) vs sampling errors (TOS errors).

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[2] This section is closely related to the theme "PAT: Process Analytical Technology vs. Process sampling" which is the topic of the forthcoming SST#4

In the current PAT focus, representativity is wholly related to spectral and reference sample measurement uncertainty (MU) and to possible data modelling errors, which unfortunately ignores the geometric specifics of sensor signal acquisition in relation to the full cross-section of the streaming/ducted flux of matter even though this is the very domain where sampling errors occur in the exact same fashion as when extracting physical samples. The process sampling interface comes to the fore.

And how does this PAT framework relates to the rock assemblages in medieval Danish churches 800 years old?

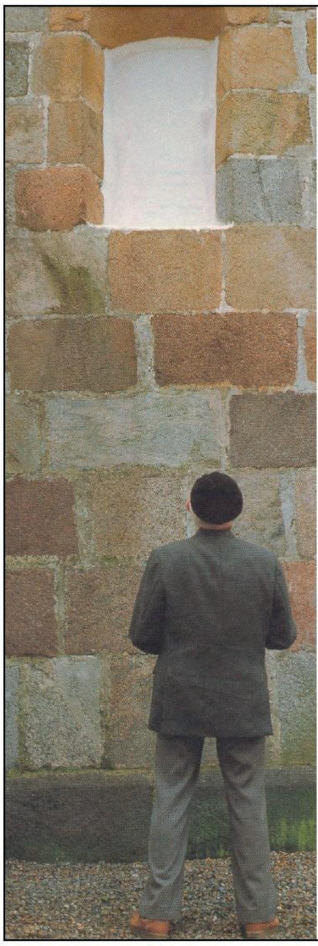
Unknowingly, Arne Noe-Nygaard devised a quite similar simultaneous sampling and analysis approach, in his case in the form of field sampling and analysis all in one. But interesting, his field sampling was not the traditional geological sample collection for analysis in the laboratory.

6. Field rock identification: field sampling and analysis in one!

So here is how Noe-Nygaard went about his analysis, i.e., visual rock type identification (aka “rock classification”), based on decades of experience with this kind of rock in Scandinavia. Noe-Nygaard was a very experienced geologist able to recognise all the seven major kinds of syenitic rocks making up the family of larvikites.

And now the story gets historical. The field sampling part (gathering the local surface rocks from the landscapes in Jutland) was undertaken by the original medieval church builders, who, with absolute certainty, were inspired and driven by very different motivations than science—masonry has it origin in the religious wish to build churches in which to worship. It was Arne Noe-Nygaard’s inspired geological brilliance to make explicit this hidden sampling aspect of medieval church building.1,2 Sampling by religious proxy! Thus, each medieval church takes on the role as a (rather large) sample of local landscape boulders, the size of which amounts to the cumulative wall area of the lowermost 5-7(8) rock courses. In passing (a treat for TOS experts), one observes that samples of this type are comprised by very, very large “particles”, making it imperative to be able to obtain a large enough square footage—the stated minimum of ca. 500 rocks.

Then, with a delay of some 800 years, fast forward to “analysis”— field rock identification (Fig. 6).



“As far as possible, I petrographically classified 500 rocks from each church involved in the investigation; this number could range between 300 and 800 depending on the local conditions (ambient light conditions, rock surface erosion, lichen overgrowth on north-facing walls). In churches with an appropriate number of available rocks, I usually restricted my work to the 4-5 lowermost rock courses. Identification of rock type up to eye-height must be considered as certain… Under less optimal conditions, classification uncertainty forced me to also observe a few courses higher up (to reach the stipulated 500 rocks). Classification certainty would in such cases have been less than normal, but still acceptable. Every year, at the start of the field campaign, I recounted ca 500 rocks in one or two of the churches visited previously without reminding myself of the earlier results.

Deviations between two such counts larger than 10% were rare.”

Figure 6: Geological maestro Arne Noe-Nygaard in the field, at work identifying (and counting) hewn rock types in a population of Romanesque medieval churches in Jutland.

From this field geological rock identification, the proportions of each larvikite rock (and, therefore, also their cumulative count) could easily be calculated as relative % w.r.t. all rocks counted for each church, which results were then plotted on a geographical map of Jutland (Fig. 7).

To close the geological part of the story, Figure 8 shows the most recent ice age glacial flow direction patterns in southern Norway. For the reader not familiar with the geography and Quaternary geology of Scandinavia, Denmark is situated some 200 km south of the Norwegian glacial flow field shown. Herewith the connection between identifiable, diagnostic erratics from the area surrounding Larvik in southern Norway and medieval church rock assemblages in Jutland, Denmark, should be fully established and understandable for all, no specialised geological competence needed.

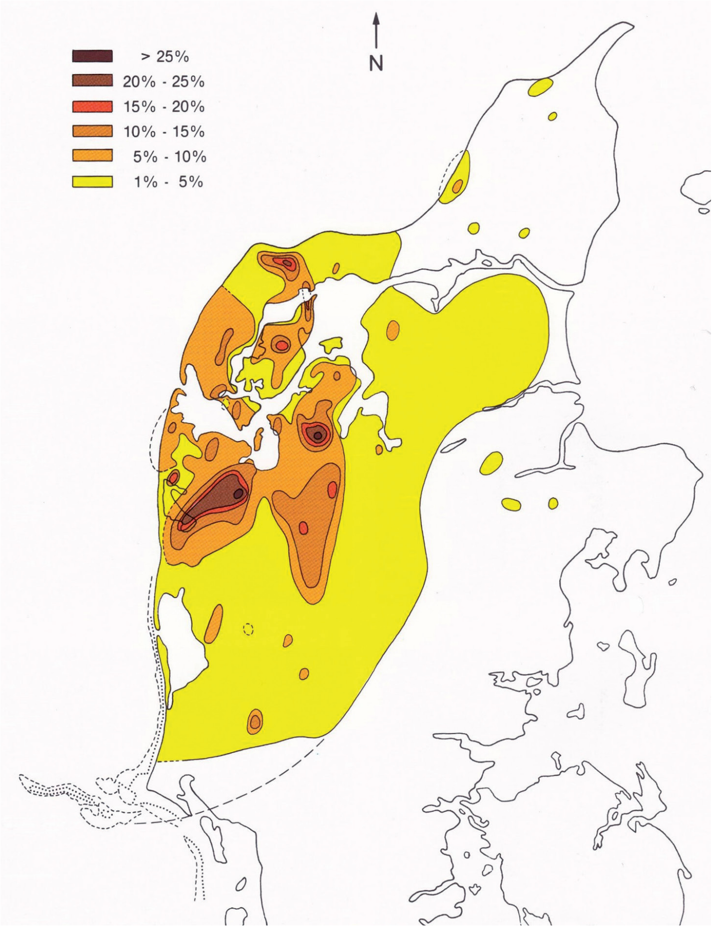


Figure 7: Relative % occurrence of larvikites (sum of all identifiable types) in Jutland hewn rock churches. The field work for this remarkable compilation was undertaken in a series of intermittent summer campaigns by Noe-Nygaard during his tenure as professor at University of Copenhagen, see Noe-Nygaard.[1,2]

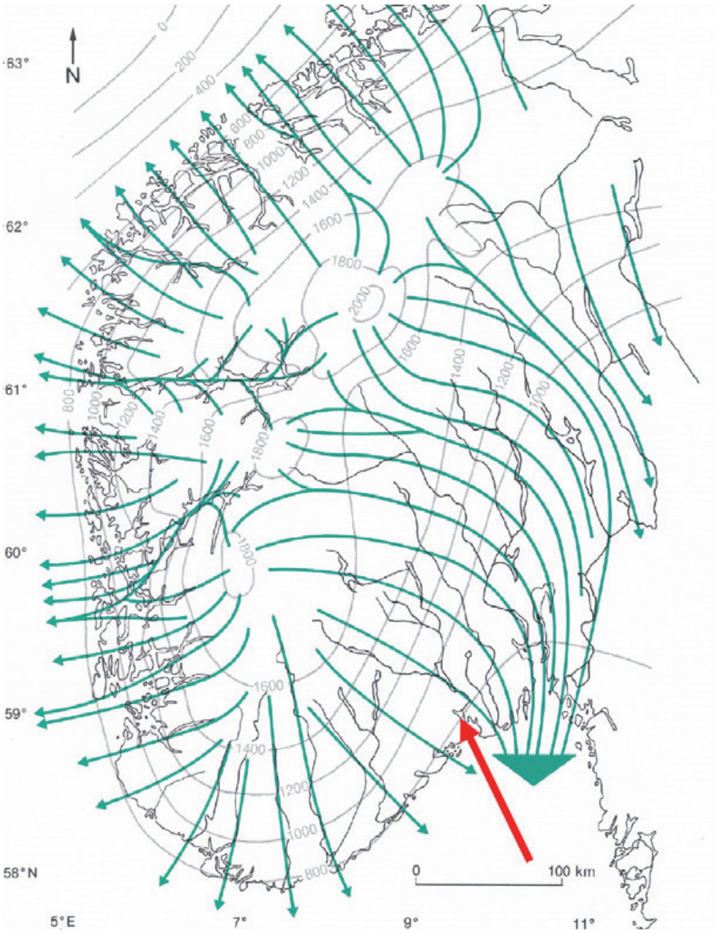


Figure 8: Ice age glacial flow direction patterns in southern Norway, see Nesje et al. (1988).[5] Contours show the modelled surface of the glacier in late-Weichsel (ca 20,00 years ago). Illustration with permission from GEUS.

7. The TOS point: the RE

The point to this extensive geological introduction is the theme of the Replication Experiment (RE), a well-known feature within TOS (Esbensen 2024).

Noe-Nygaard was acutely aware that there was an inherent "analytical error" involved in his visual identifications (TAE in today's parlance of the TOS). Such was his awareness of his analytical performance that he devised his own RE. A translation (KHE) from the Danish in Noe-Nygaard (1991) is presented in Figure 6.

This is it! What a wonderful example of a conscientious scientist, aware that his professional classification performance (analytical performance) is associated with a significant non-zero uncertainty that must be considered.

What is remarkable here is that, for geologists, the ability to identify rock types (and mineral species) is a matter of intense professional pride—this is what distinguishes a competent field geologist. One does not question a geologist's rock identification competence!

And yet, in spite of his very impressive academic a.o. achievements, Arne Noe-Nygaard's example of professional self-awareness is a remarkable, humble reminder to all scientists, technologists and samplers of today!

Credit: Anne Jodon Cole; used with permission.

Figure 9: "So how difficult can it be?" if one believes one is familiar with syenites from southern Norway, that is. The author of this article could not resist this temptation when driving past an especially inviting hewn rock church during a summer holiday in 2019. Not surprisingly, it turned out to be quite a challenge to even try to best the master geologist Noe-Nygaard's RE < 10 %.

But it is never an easy matter following the footsteps of a giant (Fig. 9), not even for a geologist familiar with igneous rocks and who has lived 10 years in Larvik! A first foray comparison of performance uncertainty (RE%), performed during a summer 2019 vacation tour in Jutland taking in a number of beautiful medieval country churches, revealed just how good Arne Noe-Nygaard was to his metier. To be honest, and to Noe-Nygaard's legacy, his "<10 %" RE uncertainty vastly outshined the score for the hopeful contemporary geologist in Figure 9 (IF the reader must ask, the answer is "a considerable larger percentage").

8. Conclusion

The RE is a very versatile facility for evaluating the total uncertainty [TSE + TAE] of any measurement system in which sampling plays a role. While RE has a plethora of manifestations within traditional sectors in technology, industry, commerce, trading and society, this column treated an unusual application of RE thinking hidden away Figure 9. "So how difficult can it be?" if one believes one is familiar with syenites from southern Norway, that is. The author of this column could not resist this temptation when driving past an especially inviting hewn rock church during a summer holiday in 2019. Not surprisingly, it turned out to be quite a challenge to even try to best the master geologist Noe-Nygaard, RE < 10 %. A famed Danish geologist devised his very own PAT-like sampling-analysis confluence spanning no less than 800 years. What's not to like?

References

[1] A. Noe-Nygaard (1991), *Larvikiter I Kvaderstenskirker. Danmarks Geologiske Undersøgelse*, Miljøministeriet, Editor Stig Schack Pedersen. ISBN 87-88640-74-4 [Danish]

[2] A. Noe-Nygaard (1985), *Kirkekvader og Kløvet Kamp*. Gyldendal. ISBN 87-00-83014-3 [Danish]

[3] K. Bakeev (2010), *Process Analytical Technology*, 2nd Edn. Wiley. ISBN 978-0-470-72207-7

[4] K.H. Esbensen and B. Swarbrick (2018), *Multivariate Data Analysis: An Introduction to Multivariate Analysis, Process Analytical Technology and Quality by Design*, 6th Ed. CAMO Software, ISBN 978-82-691104-0-1

[5] A. Nesje, S.O. Dahl, E. Anda and N. Rye (1988), Blockfields in Southern Norway: significance for the late-Weichselian ice sheet, *Norsk Geolgisk Tidsskrift 68*(3), pp. 149-169.

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Pierre Gy‘s Approach to Model the Liberation Factor

By Francis F. Pitard[1]

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ABSTRACT

Several approaches have been suggested by various authors to model the liberation factor when calculating the variance of the Fundamental Sampling Error. One of these approaches is the result of a thorough theoretical analysis and derivation authored by Dr. Pierre Gy as early as 1967.

Another approach, empirical in nature, models the liberation factor as a function of the top size of the fragments and the liberation size of the constituent of interest.

Both approaches have their respective merits. However, the empirical approach, as popular as it may be, is tampering with the theoretical integrity of Pierre Gy’s formula and may become highly misleading depending on how it is applied.

This paper emphasizes the superiority of the theoretical approach, explains the reasons why it should be the only valid approach, irrespective of some inconveniences and limitations, and finally suggests ways to eliminate the need for a liberation factor.

1. The Historical Theoretical Approach Created by Pierre Gy

The earliest publication of Dr. Pierre M. Gy is the special edition of “L’Industrie Minerale” (1967) in which the concept of the Fundamental Sampling Error (FSE) is brilliantly introduced. It is shown that FSE is the smallest possible sampling uncertainty if, and only if, for a given sample mass the conditions of equiprobability have been perfectly respected.

$$m(FSE) \approx 0 \text{ in a first order approximation} \qquad [1]$$

It is shown that the variance of FSE can be expressed as follows:

$$s^2(FSE) = \frac{1-P}{P}\sum_i\left[\frac{(a_i-a_L)^2}{a_L^2}\cdot\frac{M_i^2}{M_L^2}\right] = \frac{1-P}{P\cdot N_{Fi}}CH_L \qquad [2]$$

Where P is the sampling probability, a_i is the content of the constituent of interest in any fragment, a_L the average content of the lot to sample, M_i the mass of any fragment, M_L the mass of the lot and CH_L the Constitution Heterogeneity of the lot.

We don’t want to count the number of fragments in the lot. It is easy to overcome this difficulty by multiplying CH_L by a constant factor such as the average weight of a fragment which is by definition $\overline{M_i} = \frac{M_L}{N_{Fi}}$.
Then we have to define a new term called the *Constant Factor of Constitution Heterogeneity* IH_L also called *Intrinsic Heterogeneity* by some authors.

$$IH_L = \sum_i \frac{(a_i-a_L)^2}{a_L^2}\cdot\frac{M_i^2}{M_L} \qquad [3]$$

Therefore, the following important relation can be obtained:

$$s^2(FSE) = \frac{1-P}{P\cdot M_L}IH_L \qquad [4]$$

From this point several pragmatic formulas can be derived which have their own domain of application and limitations. For the record: there is no such thing as the Pierre Gy’s *magic* formula as is the perception given by many people around the world who are not familiar with the subtleties of his valuable work.

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[1] Francis Pitard Sampling Consultants, LLC., Broomfield, USA.

2. A pragmatic formula for a parametric approach

$$IH_L = \sum_\alpha v_\alpha \sum_\beta \rho_\beta \frac{(a_{\alpha\beta}-a_L)^2}{a_L^2} \cdot \frac{M_{L\alpha\beta}}{M_L} \quad [5]$$

The following, well-known formula is complete and still relatively simple, where α refers to a given size fraction, and β refers to a given density fraction.
The theoretical foundation of a quick approach and its limitations is the most appropriate start. Let's begin with the approximate formula used from the development of Gy's parametric approach:

$$IH_L = X \cdot Y = \left[\frac{\sum_\alpha v_\alpha \cdot M_{L\alpha}}{M_L}\right]\left[\sum_\beta \rho_\beta \frac{(a_\beta-a_L)^2}{a_L^2} \cdot \frac{M_{L\beta}}{M_L}\right] \quad [6]$$

This simplified equation is based on two important assumptions:

1. Experience shows that the content $a_{\alpha\beta}$ of a constituent of interest usually varies much more from one density fraction ß to the next than from one size fraction a to the next; therefore all the values of $a_{\alpha\beta}$ obtained in a size-density heterogeneity experiment may be replaced by the average content a_β of the corresponding density fraction L_β. This assumption is almost always true.
2. The study of a large number of real cases shows that in a size-density heterogeneity experiment the proportions $\frac{M_{L\alpha\beta}}{M_{L\beta}}$ usually varies little from one density fraction to the next; therefore, we may assume that all values $\frac{M_{L\alpha\beta}}{M_{L\beta}}$ can be replaced by their average $\frac{M_{L\alpha}}{M_L}$. This assumption may become debatable in some rare cases.

The X term is relative to the size fractions and leads to the shape factor and particle size distribution factor, while the term Y, relative to the density fractions is the one of interest in our present analysis. We know Y can be expressed as follows:

$$Y = \sum_\beta \rho_\beta \frac{(a_\beta-a_L)^2 M_{L\beta}}{a_L^2 \cdot M_L} \quad [7]$$

2.1 The mineralogical factor

Y reaches a maximum when the constituent of interest is completely liberated. This maximum is defined as the mineralogical factor c. If the material is made of only two liberated constituents, for example the gangue and the mineral of interest, then the density fraction containing the pure liberated mineral has a density ρ_M, while the gangue fraction has a density ρ_g. Then, it follows that for the fraction containing the mineral of interest the content of the mineral is $a_\beta = a_M = 1$; then for the gangue fraction $a_\beta = a_g = 0$; also the ratio $\frac{M_M}{M_L} = a_L$ and the ratio $\frac{M_g}{M_L} = (1 - a_L)$.

Transposing these values in equation [7]:

$$Y = c = \rho_M \frac{(1-a_L)^2 M_M}{a_L^2 \cdot M_L} + \rho_g \frac{(0-a_L)^2 M_g}{a_L^2 \cdot M_L}$$

After simplifications we obtain:

$$c = \rho_M \frac{(1-a_L)^2}{a_L} + \rho_g (1-a_L) \quad [8]$$

2.2 The liberation factor

Let's make several hypotheses which must be kept in mind to understand the limitations of the following recommended methods. Let's also assume we are interested in the copper content of a lot to be sampled.

First hypothesis: Following an analytical investigation, we suppose that the maximum copper content a_{max} of the coarsest fragments of the lot is known.

Second hypothesis: We suppose that all size fractions have roughly the same copper content a_L, or at least they are within the same order of magnitude.

Third hypothesis: We suppose that inside each fraction all of the copper is located in a sub fraction of copper content a_{max}, density ρ_R, and relative weight

$$\frac{M}{M_L} = \frac{a_L}{a_{\max}}, \quad [9]$$

while the remainder of the size fraction of density ρ_g,

and relative weight $1-\left(\frac{a_L}{a_{\max}}\right)$ does not contain any copper or very little.

Then we can rewrite equation [7] as follows:

$$Y = \rho_R \frac{(a_{\max}-a_L)^2 a_L}{a_L^2 a_{\max}} + \rho_g \frac{(0-a_L)^2}{a_L^2}\left(1-\frac{a_L}{a_{\max}}\right) \quad [10]$$

which leads after simplification to:

$$Y = \rho_R\left(\frac{a_{\max}}{a_L}-1\right) + (\rho_R - \rho_g)\left(\frac{a_L}{a_{\max}}-1\right) \quad [11]$$

α_{max} being usually much larger than α_L, the second term may become negligible, therefore:

$$Y = \rho_R \left(\frac{a_{\max}}{a_L} - 1 \right) \qquad [12]$$

It would be convenient to suppress the factor ρ_R which is difficult to estimate. Let's call V_1 the volume occupied by copper and V_2 the volume of the gangue. The average density ρ of their mixture can be expressed as follows:

$$\rho = \frac{V_1 \cdot \rho_M + V_2 \cdot \rho_g}{V_1 + V_2} \qquad [13]$$

with p_M being the density of the copper mineral.

But $V_1 = \frac{a_L}{\rho_M}$ and $V_2 = \frac{(1-a_L)}{\rho_g}$, then:

$$\rho = \frac{\rho_M \cdot \rho_g}{a_L \cdot \rho_g + \rho_M (1-a_L)} \quad \text{or}$$

$$\frac{\rho_M \cdot \rho_g}{\rho} = a_L \cdot \rho_g + \rho_M (1-a_L) \qquad [14]$$

By transposing [13] into the general equation [7] to calculate the mineralogical factor and after simplifications we obtain:

$$c = \frac{(1-a_L)\rho_M \cdot \rho_g}{a_L \cdot \rho} \qquad [15]$$

therefore:

$$\ell = \frac{Y}{c} = \frac{\rho_R \left(\frac{a_{\max}}{a_L} - 1 \right)}{\frac{(1-a_L)\rho_M \cdot \rho_g}{a_L \cdot \rho}} \qquad [16]$$

$$\ell = \frac{(a_{\max} - a_L)\rho_R \cdot \rho}{(1-a_L)\rho_M \cdot \rho_g} \qquad [17]$$

In practice we also know that $p_M > p_R > p > p_g$ therefore:

$$\frac{\rho_R \cdot \rho}{\rho_M \cdot \rho_g} \approx 1 \qquad [18]$$

We finally obtained the very practical formula:

$$\ell = \frac{a_{\max} - a_L}{1 - a_L} \qquad [19]$$

a_{max} and a_L should be expressed as a proportion of the copper mineral content (i.e., as part of one), and not as a metal content. This is the preferred way Pierre Gy always modelled the variability of the liberation factor for various stages of comminution.

3. Recommended method #1: Determination of a_{max} for each size fraction of a typical granulometric distribution

1. Collect a large composite sample representing a single geological unit, from leftover half core samples (e.g., fifty 6-kg samples).
2. Dry the composite.
3. Crush the composite to d = 2.54 cm. The definition of d is the size of a screen retaining no more than 5% of the material by weight.
4. Screen the entire composite using the following screens: 2.54 cm, 1.25 cm, 0.635 cm, 0.335 cm, 0.17 cm, 0.085 cm, 0.0 425cm, and 0.0212 cm. Below 0.0425 cm the method becomes very awkward but it can be done.
5. Wash, dry, and weigh each size fraction.
6. Spread the size fraction between 2.54 cm and 1.25 cm on a clean surface.
7. Using a portable X-ray machine select 10 fragments showing the highest copper content. Using a microscope, identify the main copper mineral to calculate the mineral content. Crush and grind them in a mortar, then assay them for their copper content. You obtain 10 copper results. Look at the distribution of the 10 results. Calculate the average of the 10 results and call the average an estimate of a_{max} for d = 2.09 cm. Using formula [19] calculate ℓ for d = 2.09 cm.
8. Spread the size fraction between 1.25 cm and 0.635 cm on a clean surface.
9. Using a portable X-ray machine select 10 fragments showing the highest copper content. Crush and grind them in a mortar, then assay them for their copper content. You obtain 10 copper results. Look at the distribution of the 10 results. Calculate the average of the 10 results and call the average an estimate of α_{max} for d = 1.05 cm. Using formula [19] calculate ℓ for d = 1.05 cm.
10. Repeat the same process for the other size fractions between 0.635 cm and 0.335 cm, between 0.335 cm and 0.17 cm.

11. For the smaller size fraction, identify 10 zones where the copper content is high with the X-ray machine. At each of these zones collect a spoonful of fragments. Look at them under the microscope and estimate α_{max} using proportion standard references from the mineralogist when you spot a fragment with high copper content. α_{max} will be the average of your observation from the 10 spoonful sub-samples you collected from each respective size fraction. Then, you can calculate ℓ using formula [19] for each respective size fraction.

4. Recommended method #2: Determination of α_{max} for the top size fraction of a typical comminution stage

This method is longer but may be more accurate because of the limitation of hypothesis #2 under different conditions of comminution.

1. Collect a large composite sample representing a single geological unit, from leftover half core samples (e.g., fifty 6-kg samples).
2. Dry the composite.
3. Crush the composite to d = 2.54 cm.
4. Split the composite into 7 sublots.
5. Screen one sublot using 2.54 cm and 1.25 cm screens
6. Wash, dry, and weigh the size fraction.
7. Spread the size fraction between 2.54 cm and 1.25 cm on a clean surface.
8. Using a portable X-ray machine select 10 fragments showing the highest copper content. Using a microscope, identify the main copper mineral to calculate the mineral content. Crush and grind them in a mortar, then assay them for their copper content. You obtain 10 copper results. Look at the distribution of the 10 results. Calculate the average of the 10 results and call the average an estimate of α_{max} for d = 2.09 cm. Using formula [19] calculate ℓ for d = 2.09 cm.
9. Crush the second sublot to d = 1.25 cm
10. Screen the sublot using 1.25 cm and 0.635 cm screens
11. Wash, dry, and weigh the size fraction.
12. Spread the size fraction between 1.25 cm and 0.635 cm on a clean surface.
13. Using a portable X-ray machine select 10 fragments showing the highest copper content. Crush and grind them in a mortar, then assay them for their copper content. You obtain 10 copper results. Look at the distribution of the 10 results. Calculate the average of the 10 results and call the average an estimate of α_{max} for d = 1.05 cm. Using formula [19] calculate ℓ for d = 1.05 cm.
14. Repeat the same process for the other size fractions between 0.635 cm and 0.335 cm, between 0.335 cm and 0.17 cm, by crushing another sublot appropriately each time.
15. For the smaller size fraction, after crushing a sublot appropriately, identify 10 zones where the copper content is high with the X-ray machine. At each of these zones collect a spoonful of fragments. Look at them under the microscope and estimate α_{max} using proportion standard references from the mineralogist. α_{max} will be the average of your observations from the 10 spoonful sub-samples you collected from each respective size fraction. Then, you can calculate ℓ using formula [19] for each respective size fraction.

5. The Empirical Approach Mentioned but Not Used by Pierre Gy

In Gy's earlier literature the *Constant Factor of Constitution Heterogeneity* IH_L was written as follows:

$$IH_L = f \cdot g \cdot c \cdot \ell \cdot d^3 = C \cdot d^3 \qquad [20]$$

The problem with this presentation was that C, which is the product of four factors, must be calculated every time the value of d changes since the liberation factor varies rapidly with the value of d. As a result, in the new literature it became a tradition, for practicality, to summarize the value of IH_L as follows:

$$IH_L = f \cdot g \cdot c \cdot \ell \cdot d^3 = K \cdot d^x \qquad [21]$$

In this new presentation, the liberation factor is assumed to follow an empirical model such as:

$$\ell = \left(\frac{d_\ell}{d}\right)^r \qquad [22]$$

where d_ℓ is defined as the liberation size of the constituent of interest.

In many cases when the constituent of interest is a single mineral, the exponent r is not far away from 0.5. But, as clearly shown by Gy[1] for the liberation of ash in coals, and further demonstrated by François-Bongarçon (2005) for gold, r is not necessarily anywhere close to 0.5, especially when the constituent of interest is located in various minerals.

Under such new conditions, equation [20] should be approximated as follows:

$$s_{FSE}^2 = \left[\frac{1}{M_S} - \frac{1}{M_L}\right] K \cdot d^x \qquad [23]$$

where:

$$K = f \cdot g \cdot c \cdot (d_\ell)^r \qquad [24]$$

and

$$x = 3 - r \qquad [25]$$

K and r then become the key factors to quantify in various experiments described by François-Bongarçon (2005). The author of this paper favors the approach using α_{max} for the determination of the liberation factor, in which case $x = 3$; nevertheless, François-Bongarçon's approach proved to be extremely useful in the mining industry. However, there may be a few problems when we make an attempt to compare oranges and apples, an action that may derail a so-called calibration of Pierre Gy's formula shown by equation [6].

5.1 Problems with the empirical approach

This section is a summary of Pierre Gy's philosophy well explained in his 1967 superb analysis.

The reconciliation of the theoretical approach with the empirical approach is often a complex matter. Such reconciliation is often judged very important to estimate the real value of the theoretical approach. When the difference between the theory and the real observations is too large, we can on the one hand say that the theoretical approach is incomplete or on the other hand say that the experimental observations are affected by other sources of error. It can become very difficult to analyze these annoying differences. For example, if we compare the variance of the Fundamental Sampling Error with the variance obtained from experiments, most of the time this second variance is superior to the first one. The reason is that the Fundamental Sampling Error is not the only error taking place during experiments. The conclusion is that the theoretical approach must be completed by observation from the empirical approach: both domains can complete each other if looked at it with an open mind.

The problem is that many sources of error cannot be quantified, such as variance of GSE, of IDE, of IEE, of IPE, etc. because these errors highly depend on the omnipresence of gravity generating segregation that is a transient phenomenon changing all the time.

Therefore, in the same way that some pure theoreticians refuse to account results from experiments, we may have pure empiricists discouraged by imperfect theories who find solutions with experiments and are in denial about the benefits from the theoretical analysis. Results from the empirical experiments may give us an idea about the global reality of all sources or errors; however, they are incapable of giving us logical avenues to reach all the individual causes of problems; only the theoretical approach can provide acceptable explanations.

So, going back to equations 21 through 25, it is a dangerous approach to mix oranges and apples to modify equation [5], then equation [20] (so called calibration of Gy's formula). Such practice gives a false sense of security when it is tampering with the logical rigor of the theoretical approach.

Following many years of experience the author of this paper rejects this empirical modification using equations [24] and [25] for the following reasons:

1. The sample-tree experiments lead to the cumulated variances of FSE, GSE, IDE, IEE, IPE and even AE giving no solutions for these sources of error and blaming everything on FSE.
2. When d is smaller than 1 cm, results overestimate the variance of FSE, ignoring problem with delayed comminution of the constituent of interest. Indeed, problems due to the delayed comminution of hard minerals and some soft minerals such as gold, other precious metals, molybdenite, native copper, etc. are poorly addressed.
3. When d is larger than 1 cm, results underestimate the variance of FSE, making it very difficult to represent the coarse size fractions in the collected sample. This is a huge problem.
4. It is not clear what the units are for d^{3-r}, which is an important detail.

6. Conclusions

The empirical approach strongly interferes with the integrity of Gy's formulas shown in equations [2] and [6]. As a result, it is wrong to call such approach as the "calibration" of Gy's well-known formula. Furthermore, problems with the empirical approach to calculate the liberation factor and even the theoretical approach not popular and not as well-known for most sampling theory practitioners suggest the use of a completely different approach bypassing the use of the liberation factor.

The introduction of the liberation factor concept was a magnificent academic achievement and will remain as such for those willing to use the theoretical approach. However, for those not comfortable with the current suggestions offered by both the theoretical and empirical approaches, we may suggest the following strategy that will erase any ambiguity.

7. Common Sense Suggestions

The liberation factor was an attempt to include in a single formula requirement to represent fairly all size fractions including the most difficult one to represent which is the coarse size fraction and represent also the particles of the constituent of interest. It is not a must to use the concept of liberation factor if the practitioner follows the two following Cardinal Rules.

7.1 Cardinal Rule #1: Make sure to represent all size fractions.

If the selected sample mass cannot represent all size fractions including the most difficult to represent which is the top size fraction, then the selected sample will not be representative of anything else, including the constituent of interest. Therefore, the necessary sample mass must be calculated using the following general formula suggested by Pierre Gy:

$$s_{FSE}^{2}=\left[\frac{1}{M_S}-\frac{1}{M_L}\right]f\cdot\rho\left[\left(\frac{1}{a_{Lc}}-2\right)d_{FLc}^{3}+\sum_{x}d_{FLx}^{3}\cdot a_{Lx}\right] \quad [26]$$

This formula can often be simplified for many applications:

- If $M_L > 10M_S$
- If d_{FLc} is not much different from d
- If a_{Lc} is small, then

$$s_{FSE}^{2}=\frac{f\cdot\rho}{M_S}\left[\frac{1}{a_{Lc}}-2\right]d_{FLc}^{3} \quad [27]$$

If the size fraction of interest is d which is the size opening of a screen retaining no more than 5% of the material, then the final simplified formula is as follows:

$$s_{FSE}^{2}=\frac{18\cdot f\cdot\rho\cdot d^{3}}{M_S} \quad [28]$$

7.2 Cardinal Rule #2: Make sure to represent the coarsest particles of the constituent of interest.

The following Gy's formula putting the emphasis on the constituent of interest alone can be used:

$$s_{FSE}^{2}=\left[\frac{1}{M_S}-\frac{1}{M_L}\right]\frac{f_M\cdot g_M\cdot\rho_M\cdot d_M^{3}}{a_L} \quad [29]$$

where (with subscript M referring to the Mineral of Interest):

f_M the shape factor of the constituent of interest

g_M the particle size distribution factor of the constituent of interest

ρ_M the density of the constituent of interest

d_M the maximum size of the constituent of interest particle, liberated or not, or cluster of such particles contained in a single fragment of the surrounding matrix; d_M is defined as the size of a screen that would retain no more than 5% by weight of all the particles of the constituent of interest.

Both Cardinal Rules should follow the same Data Quality Objectives (DQO), then the largest necessary sample mass obtained from these two rules must decide what the most appropriate sample mass should be.

References

Gy, P.M. (1967). *L'Echantillonage des Minerais en Vrac* (Sampling of particulate materials). Vol. 1. Revue de l'Industrie Minerale, St. Etienne, France. Numero Special (Jan. 15).

François-Bongarçon, D. (2005). The modeling of the Liberation Factor and its Calibration – *Proceedings of the Second World Conference on Sampling and Blending (WCSB2)*, 10-12 May, pp. 11-13, Sunshine Coast, Queensland, Australia, Victoria: The Australasian Institute of Mining and Minerals (AusIMM).

Recommended Recources

The following provide readers with additional historical documents dealing with more depth of the problems listed in this paper:

Gy, P.M. (1956). Poids a donner a un enchantillion-abaques, *Rev, Ind Minerale, 38*.

Gy, P.M. (1956). *Nomogramme d' echantillonage—Probenahme Nomogram*, Minerais et Metuax, Paris.

Pitard, F.F. (2019). *Sampling Theory and Sampling Practice*, (3rd ed.), Boca Raton, FL.: Taylor & Francis Group, LLC. ISBN: 13: 9781138476486.

Pitard, F.F. & Lyman , G. (2013). Single and multi-stage Poisson processes: a case for gold exploration, In J. Beniseilli, J.F. Costa, O. Dominquez, S. Duggan, K. Esbensen, G. Lyman, B. Sanfurgo (Eds.), *The Proceedings of the 6th World Conference on Sampling and Blending (WCSB6)*, 19-22 Nov. Lima, Peru, Santiago, Chile: Gecamin.

Suarez, E.V. & Carrasco, P. (2011). Numerical studies of texture and liberation in microscopic images, In the *Proceedings of the 5th World Conference on Sampling and Blending*, 25-28 Oct. Santiago, Chile, Santiago, Chile: Gecamin. ISBN: 9789568504595

Heterogeneity Characterization for Sampling Variance Prediction

By Dominique François-Bongarçon[1]

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1. Gy‘s Formula and The Liberation Factor

As mentioned in a more comprehensive contribution at WCSB11 (Francois-Bongarcon, 2024), the analytical model proposed by Gy for *fully liberated* materials was as follows:

$$\text{Rel.Var.} = cfgd^3_{95}\,(1/M_S - 1/M_L) \quad (1)$$

(for liberated, comminuted, or naturally occurring particulate material)

In this formula, only some parameters can be set at the sampling time: the sample mass Ms, and the comminution P_{95} size d_{95}. Other parameters can be calculated from known properties of the material to be sampled: the mineralogical constant c, the shape factor f, and the granulometric factor g.

The restriction of the formula to fully liberated materials was an obvious impediment to using it for practical predictions of sampling variances in general cases. Gy therefore offered a modified version:

$$\text{Rel.Var.} = c\,\ell\,fgd_{95}{}^{3}\,(1/M_S - 1/M_L) \qquad (2)$$

in which a ‚liberation factor‘, ℓ (numerical values between 0 and 3) was introduced to account for the degree of non-liberation of the material. No acceptable and practical working model was offered for this factor ℓ until the present author’s work in the 90’s.

To conform with Gy‘s intuitions about ℓ being directly correlated to the proportion of liberated material and to additional De Wijsian geostatistical considerations, the fractal, heuristic model then proposed:

$$\ell = (d_\ell \,/\, d\,)^b \qquad (3)$$

introduced two more parameters in formula (2):

- a De Wijsian exponent, b, which is linked to the model of clustering of the pure analyte particles in the gangue, and
- a particle size parameter d_ℓ often likened to the analyte ‘particle liberation size’.

Heterogeneity characterization studies aim at finding the best values for these parameters to successfully customize formula (2) for the material at hand. A comprehensive overview of the critical conceptual assumptions and practical technical issues that must be observed was given by Chieregati (2024).

THE STUDY OF HETEROGENEITY

Pierre Gys‘ legacy includes not only the most impressive synthesis of the first principles that will guarantee successful use of sampling for a variety of applications, but also a numerical model aimed at helping the practitioner accurately predict sampling precision from sampling parameters. Naturally, this step implies a customization of the analytical model of variance, often known as ‘Gy‘s formula’. This customization is often coined ‘heterogeneity study’, and is always aimed at predictions and the solving of what-if scenarios.

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[1] Agoratek International Consultants Inc., Canada.

2. A Simple, Fundamental Remark

The analytical simplicity of these models is deceptive, but their calibration is a critical success factor of great importance. Indeed, a poor calibration, especially of the De Wijsian exponent, may easily result in grossly optimistic, or pessimistic, variance predictions. In the first case, enormous amounts of money may be lost in the long run depending on the application (e.g., grade control in a mine). In the second, huge capital money may be wasted (e.g. over-dimensioning of sampling preparation laboratories). The importance of properly performing heterogeneity characterizations cannot be under-estimated. Ad hoc methods, simplifications and all-made recipes are dangerous and should be avoided for this delicate purpose.

This said, that importance is often obfuscated by false debates between specialists. While some, with us, do advocate carefully performed heterogeneity studies using proper, non-liberated models, other think they are either invalid in their essence, too complex to be performed well, or even useless. This author strongly believes these discussions to be irrelevant, because they invariably take place between practitioners who reason in completely different contexts and with non-comparable objectives: characterizing a given situation versus predicting what-if scenarios.

In the case of an open pit mine with blast hole sampling, the basis of grade control, for instance, very distinct problems can be considered.

- The sole determination of the minimum sample mass to reach a desired precision does not require the full models of formulas (2) and (3) above and instead can be solved with a simple sampling experiment.
- Conversely, the dimensioning and capital optimization of a sample preparation laboratory to process the samples once they are collected, would clearly imply the prediction of a variety of possible sub-sampling stages scenarios, with several hypothetical variations in comminution sizes (and therefore in states of liberation), rendering necessary the use of a model for the liberation factor.

Finally, humility is required. One cannot lightly criticize models that, properly applied, have successfully received Georges Matheron's criterion of the 'sanction of practice' over a period of more than 30 years (Matheron, 1989).

3. Recommendations

After describing common heterogeneity characterization practices, the above-referenced WCSB11 paper lists a series of Do's and Don'ts to help the practitioner perform meaningful calibrations. We only need to repeat/enhance them here, to make the present short communication a flag-waiving referral companion to the 2024 WCSB11 paper.

3.1 Do's

- Perform a careful analysis of all available data: are they representative of the sampling case that needs to be performed?
- Try to determine which type of material (e.g., mineralization type) gives the *worst* response to sampling – then focus on this case.
- Try to objectively eliminate outlying data without letting that operation bias the final results. There is no doubt that this issue demands the largest possible experience: Don't do this on you own, if you are not competent – Do contact experienced colleagues or consultants.
- Understand fully the issue at stake, especially the economic consequences of the heterogeneity calculations, and the most critical aspects of their applications.
- Take your time: these are delicate empirical operations; they need to be performed with an intimate understanding of what needs to be properly achieved.
- Formula (2) is for a single stage of sampling, and not, as would the case be for the variance calculated from the grades of routine samples, the variance of a full series of cascading sampling operations alternated with comminution stages. Therefore, when using one of the methods involving splitting of a series of samples, make sure the experiment is properly designed so that the variances calculated from laboratory assay results can be 'cleaned up' before being equated to formula (2). In other words, one must be able to remove unwanted variance components from the results (such as those due to subsequent preparation and sub-sampling on top of the primary sampling operation). This, and only this, will allow to correctly equate the sampling formula (2) to the result of a resulting single-stage, primary sampling operation. In particular, in a simple case where the samples in one series are only pulverized and assayed after being collected, then removing the pulp sampling and analytical variances from the total assay variance requires that one of the available series be a series of samples taken from already pulverized material.

Not removing that component will always give a high-biased value of De Wijsian exponent b, with an enormous effect on predicted sampling variances.

- The splitting methods used to generate a series of samples *should* give random samples reasonably protected from the effects of natural segregation. Riffle splitting, alternate shoveling and fragment-per-fragment selection are the recommended methods. Rotary splitters, on the other hand, do not give random samples and can therefore not be used to calibrate a theoretical formula they have nothing to do with. When this difference was discussed with Pierre Gy, he told the author of this paper that the difference between random and rotary sampling was akin to the difference between dealing a thoroughly shuffled deck of cards (riffling or random sampling) and to doing so after carefully sorting the deck by color and card values (rotary splitting). Indeed, to the usual surprise of many a practitioner, that method (rotary splitting), a circular version of bed-blending, uses segregation as an advantage. Any segregation aggregates that pass through the system is falling into the containers of the carousel in such a way that it is uniformly distributed in them, a feat that cannot be achieved by random sampling of any kind. Segregation in that process, contrary to the case of random sample selection (e.g., in random increments); therefore, is an additional, favorable feature for the division. Thus, segregation is used to the advantage of representativeness, to such a point that the corresponding sampling errors have variances potentially much lower than those of regular random sampling, i.e., lower than predicted by TOS formulas.
- If the calibration uses a graphical approach, care should be taken to make sure the quantities plotted together on the same calibration graph were made directly comparable/compatible (i.e., representing the same quantities as a function of the abscissa). To achieve this, instead of plotting only the 'Rel.Var.' quantity of formula (2) as a function of d95, the plotted quantity should absorb any factor of difference. For instance, if two points on the graph correspond to: i) sampling of closely sieved material, and ii) sampling a full-size distribution of material, then the plotted quantity should be first divided by the respective granulometric factors g and g'. If various points have different grades, the quantity should also be divided by 'c' (which is a function of grade) before plotting it.

3.2 Don‘ts

- First of all, don‘t fall victim to ready-made, ad hoc formulas and nomograms that were published in the past (more particularly pre-1992), they simply will not work.
- Don‘t over-trust QA/QC duplicate sample results. Such duplicate samples were manifestly not collected for this purpose, and they are often consciously or unconsciously *doctored*, by removing parts of what needs to be quantified. Indeed, it is standard and normal for a laboratory manager to review the assays before they are delivered to the laboratory's client. However, any duplicate result deemed abnormal in his/her own judgement or intuition (eventually ill-informed) will be removed, factored or redone.
- Be keenly aware of the differences between *sampling* (TOS) and *measuring* (geostatistics), between samples and measurement supports and therefore do not use measurement support duplicates (i.e., repeats of some in-situ sampling, such as *duplicate* channel samples or *duplicate 1/2 core* as a mere examples).
- Of course, the samples should be able to represent TOS formula (2) for random samples, which precludes using non-random splitters such as rotary ones.
- The parameters obtained should ultimately be compatible with the sampling procedures to design, diagnose, or optimize. In particular, sampling characteristics of a lot of comminuted material simply cannot be derived for a single size-fraction, which, alone, may easily have different sampling properties than the whole.

4. Conclusion

While heterogeneity studies may appear somewhat complex at first sight, they are not ‚rocket science‘ – but they must be performed very carefully with full acknowledgement of the specific experimental conditions, as their economic impact can be devastating if they are strongly biased. The present author has treated the topics covered above on several occasions since 1992. More comprehensive analysis, argumentation, and documentation can be found in the bibliography below.

References

François-Bongarçon, D. (2024). Heterogeneity Studies: Do‘s and Don‘ts. *The Proceedings the World Conference on Sampling and Blending 11*, May 21-23, Misty Hills Conference Center, Muldersdrift, Johannesburg, South Africa, The Institute of Mining and Metallurgy (SAIMM), pp. 15-24. ISBN: 978-1-7764673-0-3, https://www.saimm.co.za/Conferences/files/wcsb11-2024/02_WCSB649-Francois-Bongarcon.pdf

Chieregati, A.C. (2024, Nov.). A Brief Review of Heterogeneity Tests for Estimating the Variance of the Fundamental Sampling Error. *Sampling Science & Technology Magazine*, 2, pp.19-29, DOI: 10.62178/sst.002.003, https://www.sst-magazine.info/wp-content/uploads/2024/11/sst-002-003.pdf

Matheron, G. (1989). *Estimating and Choosing: An Essay on Probability in Practice*, A.M. Hafsofer (trans.), Springer-Verlag, Berlin, New York, London, Paris. DOI:10.1007/978-3-642-48817-7

Bibliography

François-Bongarçon, D. (1992). Geostatistical Tools for the Determination of Fundamental Sampling Variances and Minimum Sample Masses, *Proceedings of Geostatistics Troia ‚92. Kluwer Academic Pub.* 2, Troia, Portugal, pp. 989-1000.

François-Bongarçon, D. (2008). Sampling and Heterogeneity Studies Creative Methods. *Proceedings of W Sampling Conference*, 27-29 May, Perth, W. AUS., Victoria, AUS: Australasian Institute of Mining and Metallurgy (AusIMM) pp.67-68, ISBN: 978 1 920806 81 1

François-Bongarçon, D. (2017). The evolution of the concept of liberation factor and a surprising new result. In S. Dominy & K.H. Esbensen (Eds.), *Proceedings of Eighth World Conference on Sampling and Blending*, 9-11 May, Perth, W.AUS., Victoria, AUS.: Australasian Institute of Mining and Metallurgy (AusIMM), pp. 307-310, ISBN: 978 1 925100 56 3

François-Bongarçon, D. (2022). Liberation factor for ‚closely sieved‘ material. In K. H. Esbensen & A.J. Cole (Eds.), *Proceedings of Tenth World Conference on Sampling and Blending*, 31 May - 2 June, Kristiansand, NO., *TOS forum 11*, Chichester, UK.: IMpublication Open LLP, pp. 7-9. doi:10.1255/tosf.xxx

François-Bongarçon, D. & Gy, P. (2002). The Most Common Error in Applying ‚Gy‘s Formula‘ in the Theory of Mineral Sampling, and the History of the Liberation Factor. *The Journal of The South African Institute of Mining and Metallurgy*, Nov./Dec. https://www.saimm.co.za/Journal/v102n08p475.pdf

François-Bongarçon, D. & Pitard, F. (2015). Comparison between samples with constant mass and samples with constant fragment population size, In *Proceedings of Seventh World Conference on Sampling and Blending*, K. H. Esbensen & C. Wagner (Eds.), 10-12 June, Bordeaux, FR. *TOS forum 5*, Chichester, UK.: IMpublication Open LLP, pp. 231-238. ISSN: 2053-9681.


TOXICOWATCH

Giants of Sampling 3: Sylvanus Albert Reed

By Alan F. Rawle[1]

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1. The very first step towards representative sampling?

S(ylvanus) Albert Reed's claim to fame is that he probably laid down in print the first mathematical formula concerning representative sampling. As such he must certainly be counted among the founding fathers of what later came to be known as the Theory of Sampling (TOS). We'll deal with this formula in a later section, noting that this contribution was minor in respect of all else he achieved. We can compare him with Brunton (Giants of Sampling #2, in SST#2) in many ways possessing a wide range of skills and accomplishments. He made his money in a field outside mining (some cynics would claim that making a fortune in mining isn't possible). He bridged the academic Holy Grail: From an initial degree in arts, his course took him through science and engineering and into the money. Initially he pursued a career in mining, but this gave way to work in the insurance field, electrical signaling for railways, and general chemistry patenting, specifically an invention in generating electricity from coal gas culminating in the invention of the first sustainable metal aircraft propeller. Like Brunton (see issue 2 of SST), he patented then defended his patents extensively. In the compilation of literature available, his preferred form of address was S. Albert Reed, so we can deduce that (like many others) he was not fond of his given first name and preferred Albert (or perhaps Bert/Bertie?).

2. Family

Sylvanus Albert Reed was born on the 8th April, 1854, in Albany, New York, United States. His father was the Reverend Sylvanus S. Reed (13th July, 1821 – 16th October, 1870) and his mother was Caroline (Gallup) Reed.

Sylvanus Albert Reed was married only once (when he was an insurance executive) and, sadly, the duration was short-lived as his wife, Elmina Wilshire Pomeroy (known as Ella or Ellen) died just after their second anniversary.

EDITOR'S NOTE

Nowadays, Alan is on his own recognizance but scientifically is not at all retired. He continues his magisterial series on "Giants on Sampling" this time on the history of one of sampling's lesser known (very) early initiators.

3. Education

We are lucky to be able to trace Reed's education and early career through Alumni publications of the Columbia School of Mines. Prior to college, he was educated in various public and private schools including Albany Academy and several New York schools. Eventually he obtained five degrees!

- AB (1874) – an arts undergraduate degree, Columbia University
- AM & ME (1877) – degrees from the School of Mines, Columbia University
- Ph.D. (1880) "The investigation of Professor Mayer's method of locating wave surfaces in media surrounding sounding bodies", Columbia University
- D.Sc (1929) – this was honorary in relation to his later aeronautic/propeller work

The Columbia University Class of 1874 Yearbook contains two wonderful pictures of Reed aged around 20 (Fig.1). In 1899, at the 25th Anniversary reunion provides another picture of Reed aged around 45 years old (Fig 2).

He made his contribution to sampling with two papers, one in 1882 and the other in 1885. However, in 1886 he made a switch from mining to Insurance Engineering, which appears to be quite a move. He specialized in electrical signals for railroad safety and patented extensively in this period. His major insurance work was the classic report on the 'San Francisco Fire/Conflagration (1906)', which followed the earlier earthquake.

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[1] Retired. Hardwick, Massachusetts, USA.

Figure 1: Photos of Sylvanus Albert Reed (age ~20) at Graduation. Courtesy of Columbia University Archives.

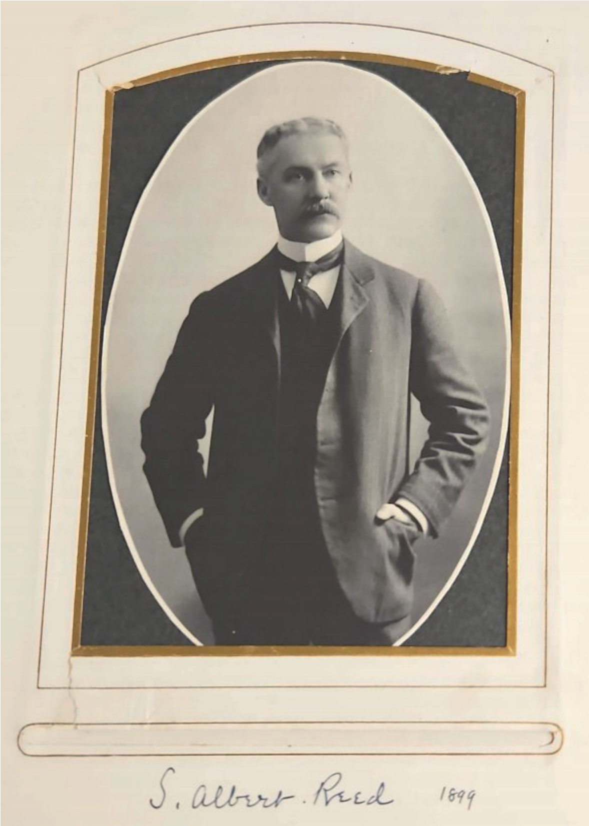


Figure 2: Sylvanus Alvert Reed at the 1899 college Class Reunion (age ~45). Courtesy of Columbia University Archives.

4. Sampling

Sylvanus Albert Reed published two papers on sampling in The School of Mines Quarterly in 1882 and 1885 respectively, surprisingly not based on his Ph.D. thesis of 1880. Although he had no further academic activity in the field, he held some jobs in mining and sampling works that are documented in the Columbia University Alumni publications before his move into insurance.

5. In medias res

His first paper in 1882, entitled simple "Ore Sampling", is a just a little over seven pages long. It is rather general and descriptive. Early on he remarks, prescient to Pierre Gy, "Exact sampling must be assured, or a bid becomes merely a bet". He further states that "the subject (*sampling*) has been more scientifically studied and carried nearer perfection in Colorado than anywhere else". This indeed reflects the emphasis on gold and silver ores in the mining papers around that time. He takes around three pages to describe his preferred method (probably used when he was employed in the field) involving crushing and (split) shoveling reducing 10 tons to 1 ton, eventually ending up with three samples (buyer, seller, referee/umpire) passing 80 mesh (~ 180 microns) of about ¾'s of a pound (~ 340 g).

He displays a figure illustrating the ‘automatic part’ of his sampling process from which it is quite clear that this type of riffling process is subject to what TOS today would label as ‘delimitation errors’:

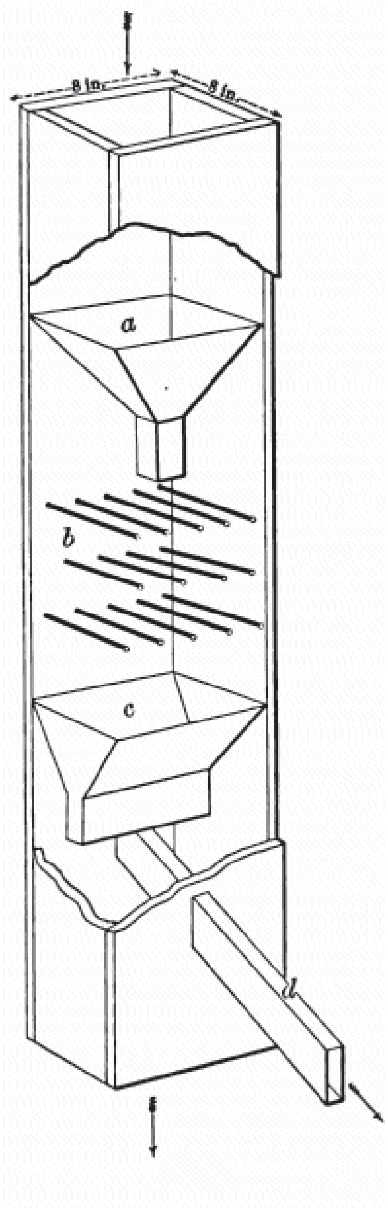


Figure 3: The “Reed 1882 Automatic Sampler”

We are informed that the rods (‘b’ in the diagram) are there to “thoroughly mix the starting material” while at the bottom of chute ‘c’ one-tenth of the material is extracted only from the center of the chute along the inclined plane, ‘d’. This is where the claim to ‘representative sampling’ is certainly not justified. Reed comments “It would be an interesting problem to work out mathematically from the doctrine of *chances*, the principles of good sampling of an irregular mixture”.

He explores this mathematics in his 1885 paper. However, in his 1882 paper, Reed gives four fundamental points regarding sampling that can be summarized as:

- A certain maximum limit in the sample to the ratio between coarseness and quantity (of sample to be extracted). This is related to the top particle size (x_{95} or x_{99} in modern literature)
- Minimum mass of sample to be extracted from the whole
- No selectivity in sampling – “free from any tendency to select one set of particles at the expense of others
- Thorough mixing, and no tendency for sorting

The 1885 paper: “More remarks on Ore Sampling” begins by stating three important principles:

1. Adequate mixing
2. Impartial selection
3. Proper relative comminution

He then states the important maxim: “In fact, it may be stated that the probable error in properly conducted ore sampling operations is less than the probable error of the assay of the sample when obtained”, a fact ‘known’ (‘felt’) to be true for many years.

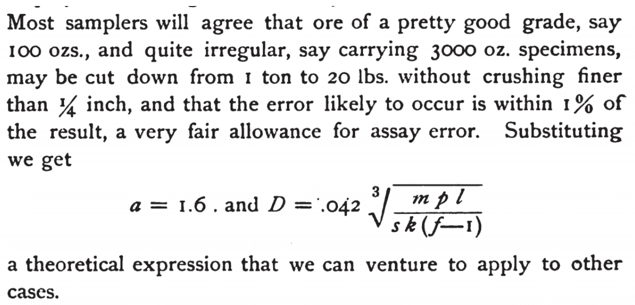
Reed describes a number of forms (modes) of sampling from quartering to mechanical means concluding that of the mechanical methods “*The latest and best is that of Mr. Brunton, described in a recent paper read before the Am. Inst. of Mining Engineers*”. However, he is also quick to criticize Brunton: “*Mr. Brunton, by the way, in his paper makes the misleading statement that the bulk of Colorado ore is sampled mechanically, whereas I will venture to say that 3/4 of the ore product of that State is sampled by hand*”, a personality trait (mild autism/Asperger’s)? that we can observe throughout his literature and interactions with authorities. Reed then begins the most important part of this landmark paper by stating:

The divergence of any portion of a lot of ore from the average percentage composition of the whole is due to the excess or deficit of one or more particles. The effect upon the result will be greatest when the pieces causing this divergence are of the largest size and richest quality.

He then defines a number of terms:

p = the quantity of the lot (in Troy ounces)
f = the number of parts into which we divide before selecting one as sample
k = percentage (of silver or gold in the *richest* specimens in the lot)
s = sp. gr. of the same
m = the *grade* of the ore in ozs., per ton
D = diameter of *largest pieces* in the lot in inches
a = the number of pieces of size D, and k value, that can be in excess or deficit in the portion chosen for sample

Working in the above units provides some conversion difficulties. However, Reed does end up with a practical formula:



Most samplers will agree that ore of a pretty good grade, say 100 ozs., and quite irregular, say carrying 3000 oz. specimens, may be cut down from 1 ton to 20 lbs. without crushing finer than ¼ inch, and that the error likely to occur is within 1% of the result, a very fair allowance for assay error. Substituting we get

$$a = 1.6 \text{ . and } D = .042 \sqrt[3]{\frac{m\,p\,l}{s\,k\,(f-1)}}$$

a theoretical expression that we can venture to apply to other cases.

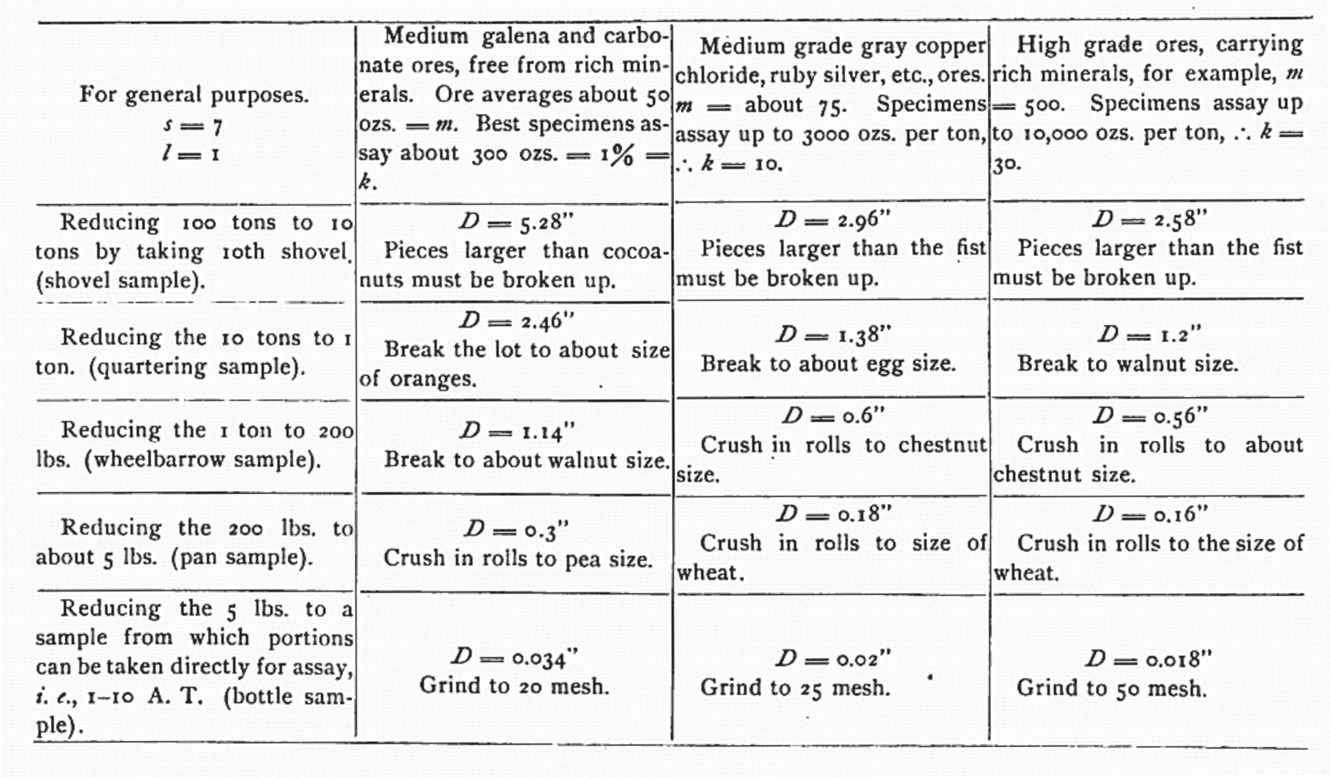
Figure 4: The "Reed Formula 1885"

He is then able to provide an important summary table indicating the particle size to which certain ores need to be comminuted (see Fig. 5).

We note the reduction starting from 100 tons down to 5 pounds and then ground below a certain mesh size for a laboratory assay sample. This is the classic chart and was used for the basis of a very similar chart in various of Heinrich O(scar) Hofman's texts. Hofman was the second MIT mining professor after the first, Robert Hallowell Richards, who will be the next Giant of Sampling in this series.

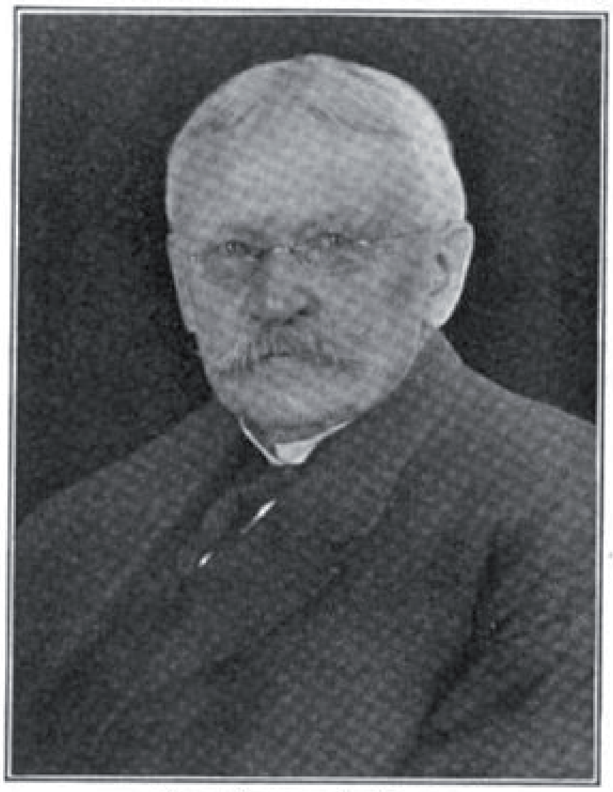
It is interesting to note Hofman's estimated costs and their breakdown for the summer school. The Board and Lodging is attributed to $1.50/day for 24 days making a total of $36, while the rail fares for the journeys including to and from Boston total $35. Washing and sundries make up $9. One wonders what comparable costs would be nowadays.

Hofman is responsible for attributing some important sampling generalities to Henry Vezin: "Vezin, in 1866, finding that with pyritic ores of Gilpin County, Colo. , running from 1 to 4 oz. of gold per ton, it was safe to cut down to 1 oz. a sample that had passed a 20-mesh screen, the diameter of the largest particle being 1 mm (1/25 inch) prepared the following table for this class of ores" (see Fig. 8).



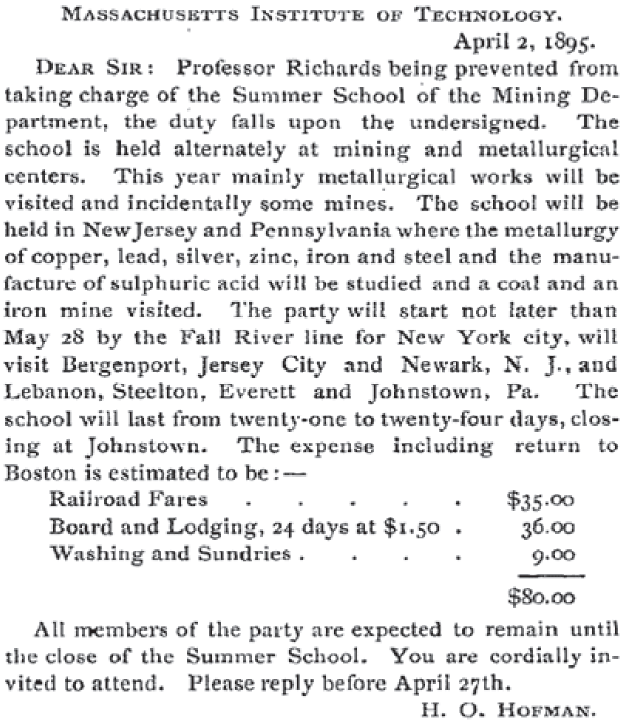
For general purposes. $s = 7$ $l = 1$	Medium galena and carbonate ores, free from rich minerals. Ore averages about 50 ozs. $= m$. Best specimens assay about 300 ozs. $= 1\% = k$.	Medium grade gray copper chloride, ruby silver, etc., ores. $m =$ about 75. Specimens assay up to 3000 ozs. per ton, $\therefore k = 10$.	High grade ores, carrying rich minerals, for example, $m = 500$. Specimens assay up to 10,000 ozs. per ton, $\therefore k = 30$.
Reducing 100 tons to 10 tons by taking 10th shovel (shovel sample).	$D = 5.28''$ Pieces larger than cocoanuts must be broken up.	$D = 2.96''$ Pieces larger than the fist must be broken up.	$D = 2.58''$ Pieces larger than the fist must be broken up.
Reducing the 10 tons to 1 ton. (quartering sample).	$D = 2.46''$ Break the lot to about size of oranges.	$D = 1.38''$ Break to about egg size.	$D = 1.2''$ Break to walnut size.
Reducing the 1 ton to 200 lbs. (wheelbarrow sample).	$D = 1.14''$ Break to about walnut size.	$D = 0.6''$ Crush in rolls to chestnut size.	$D = 0.56''$ Crush in rolls to about chestnut size.
Reducing the 200 lbs. to about 5 lbs. (pan sample).	$D = 0.3''$ Crush in rolls to pea size.	$D = 0.18''$ Crush in rolls to size of wheat.	$D = 0.16''$ Crush in rolls to the size of wheat.
Reducing the 5 lbs. to a sample from which portions can be taken directly for assay, *i. e.*, 1–10 A. T. (bottle sample).	$D = 0.034''$ Grind to 20 mesh.	$D = 0.02''$ Grind to 25 mesh.	$D = 0.018''$ Grind to 50 mesh.

Figure 5: Size to which various ore types need to be comminuted – "The Chart"



Prof. Heinrich O. Hofman.

Figure 6: Heinrich Hofman



MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

April 2, 1895.

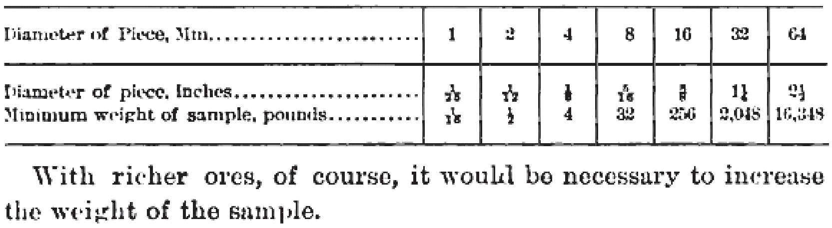
DEAR SIR: Professor Richards being prevented from taking charge of the Summer School of the Mining Department, the duty falls upon the undersigned. The school is held alternately at mining and metallurgical centers. This year mainly metallurgical works will be visited and incidentally some mines. The school will be held in New Jersey and Pennsylvania where the metallurgy of copper, lead, silver, zinc, iron and steel and the manufacture of sulphuric acid will be studied and a coal and an iron mine visited. The party will start not later than May 28 by the Fall River line for New York city, will visit Bergenport, Jersey City and Newark, N. J., and Lebanon, Steelton, Everett and Johnstown, Pa. The school will last from twenty-one to twenty-four days, closing at Johnstown. The expense including return to Boston is estimated to be:—

Railroad Fares	$35.00
Board and Lodging, 24 days at $1.50 .	36.00
Washing and Sundries	9.00
	$80.00

All members of the party are expected to remain until the close of the Summer School. You are cordially invited to attend. Please reply before April 27th.

H. O. HOFMAN.

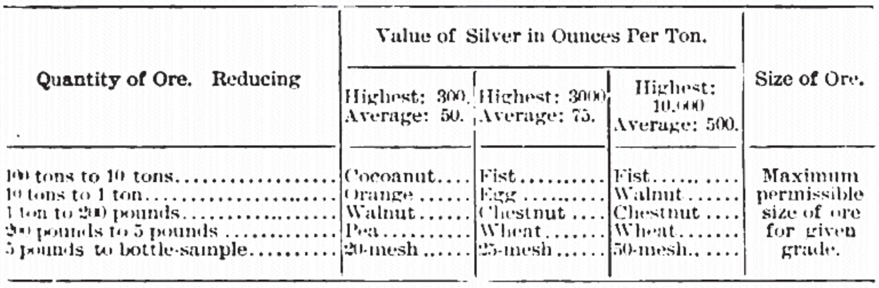
Figure 7: Summer school costs after Hofman (source unknown)



Diameter of Piece, Mm.	1	2	4	8	16	32	64
Diameter of piece, Inches	1/25	1/12	1/6	5/16	5/8	1 1/4	2 1/2
Minimum weight of sample, pounds	1/16	1/2	4	32	256	2,048	16,348

With richer ores, of course, it would be necessary to increase the weight of the sample.

Figure 8: Vezin's Table (according to Hofman)

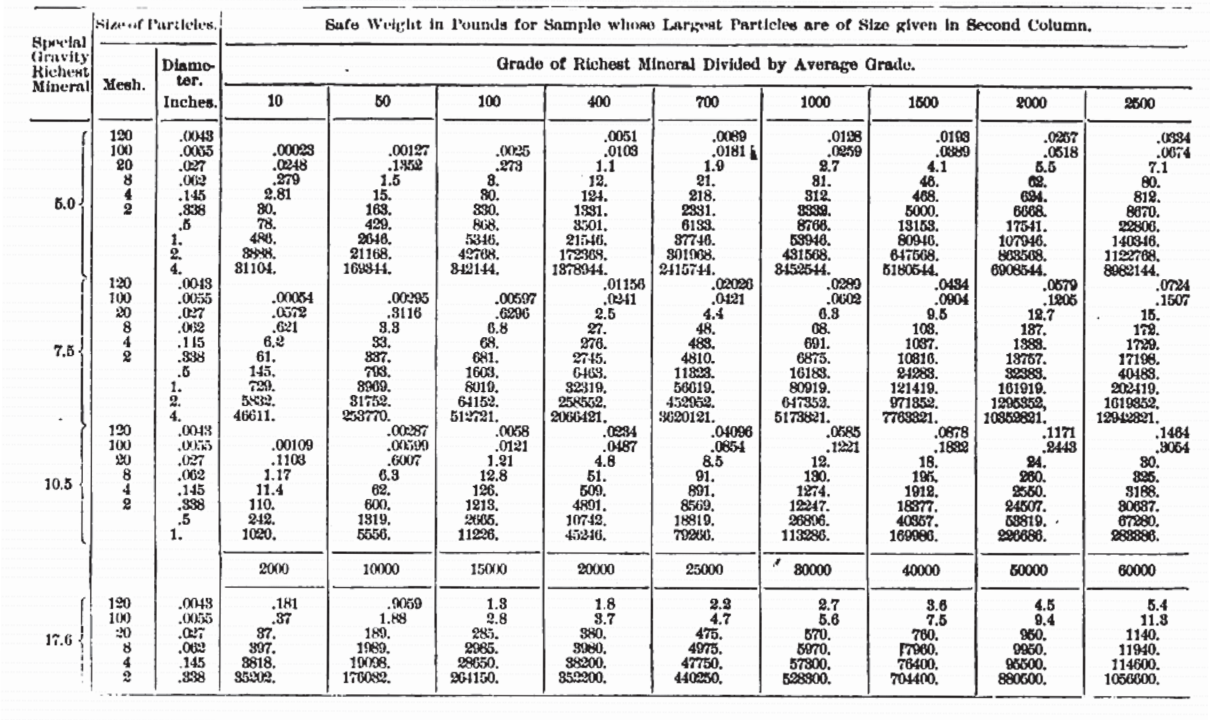


Quantity of Ore. Reducing	Value of Silver in Ounces Per Ton.			Size of Ore.
	Highest: 300. Average: 50.	Highest: 3000. Average: 75.	Highest: 10,000 Average: 500.	
100 tons to 10 tons	Cocoanut	Fist	Fist	Maximum permissible size of ore for given grade.
10 tons to 1 ton	Orange	Egg	Walnut	
1 ton to 200 pounds	Walnut	Chestnut	Chestnut	
200 pounds to 5 pounds	Pea	Wheat	Wheat	
5 pounds to bottle-sample	20-mesh	25-mesh	50-mesh	

Figure 9: Hofman's summary of Reed's original table

It seems unlikely that this work can date back as far as 1866 given that Vezin was living in Philadelphia at that time and had not yet moved west to Colorado. Hofman then talks of Reed's calculation and provides a smaller and amended table to that of Reed's above (see Fig. 9).

Hofman further expands the discussion by working with some of Brunton's material that was discussed in the "Giants of Sampling 2" article. He shows a table developed for him by a certain Mr. Fr. Drake showing the minimum weights of sample needed for crushing different ore types as examples (pyrites, silver, gold – see Fig. 10).

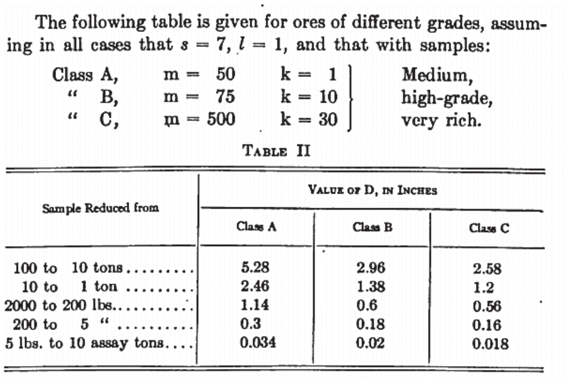


Special Gravity Richest Mineral	Size of Particles. Mesh.	Diameter. Inches.	Safe Weight in Pounds for Sample whose Largest Particles are of Size given in Second Column.								
			Grade of Richest Mineral Divided by Average Grade.								
			10	50	100	400	700	1000	1500	2000	2500
5.0	120	.0043				.0051	.0089	.0128	.0198	.0257	.0334
	100	.0055	.00023	.00127	.0025	.0103	.0181	.0259	.0389	.0518	.0674
	20	.027	.0248	.1352	.273	1.1	1.9	2.7	4.1	5.5	7.1
	8	.062	.279	1.5	3.	12.	21.	31.	46.	62.	80.
	4	.145	2.81	15.	30.	124.	218.	312.	468.	624.	812.
	2	.338	30.	163.	330.	1331.	2331.	3339.	5000.	6668.	8670.
		.5	78.	429.	868.	3501.	6133.	8766.	13153.	17541.	22806.
		1.	486.	2646.	5346.	21546.	37746.	53946.	80946.	107946.	140346.
		2.	3888.	21168.	42768.	172368.	301968.	431568.	647568.	863568.	1122768.
		4.	31104.	169344.	342144.	1378944.	2415744.	3452544.	5180544.	6908544.	8982144.
7.5	120	.0043				.01156	.02026	.0289	.0434	.0579	.0724
	100	.0055	.00054	.00295	.00597	.0241	.0421	.0602	.0904	.1205	.1507
	20	.027	.0572	.3116	.6296	2.5	4.4	6.3	9.5	12.7	15.
	8	.062	.621	3.3	6.8	27.	48.	68.	103.	137.	172.
	4	.115	6.2	33.	68.	276.	483.	691.	1037.	1383.	1729.
	2	.338	61.	337.	681.	2745.	4810.	6875.	10316.	13757.	17198.
		.5	145.	793.	1603.	6463.	11323.	16183.	24283.	32383.	40483.
		1.	729.	3969.	8019.	32319.	56619.	80919.	121419.	161919.	202419.
		2.	5832.	31752.	64152.	258552.	452952.	647352.	971352.	1295352.	1619352.
		4.	46611.	253770.	512721.	2066421.	3620121.	5173821.	7763321.	10352821.	12942821.
10.5	120	.0043		.00287	.0058	.0234	.04096	.0585	.0878	.1171	.1464
	100	.0055	.00109	.00599	.0121	.0487	.0854	.1221	.1832	.2443	.3054
	20	.027	.1103	.6007	1.21	4.8	8.5	12.	18.	24.	30.
	8	.062	1.17	6.3	12.8	51.	91.	130.	195.	260.	325.
	4	.145	11.4	62.	126.	509.	891.	1274.	1912.	2550.	3188.
	2	.338	110.	600.	1213.	4891.	8569.	12247.	18377.	24507.	30637.
		.5	242.	1319.	2665.	10742.	18819.	26896.	40357.	53819.	67280.
		1.	1020.	5556.	11226.	45246.	79266.	113286.	169986.	226686.	283386.
			2000	10000	15000	20000	25000	30000	40000	50000	60000
17.6	120	.0043	.181	.9059	1.3	1.8	2.2	2.7	3.6	4.5	5.4
	100	.0055	.37	1.88	2.8	3.7	4.7	5.6	7.5	9.4	11.3
	20	.027	37.	189.	285.	380.	475.	570.	760.	950.	1140.
	8	.062	397.	1989.	2985.	3980.	4975.	5970.	7960.	9950.	11940.
	4	.145	3818.	19098.	28650.	38200.	47750.	57300.	76400.	95500.	114600.
	2	.338	35202.	176082.	264150.	352200.	440250.	528300.	704400.	880500.	1056600.

Figure 10: Hofman's Table based on Brunton calculations

Obviously, this is a fairly complex table. The rest of Hofman's sampling chapter deals with the classic sampling methods – quartering, shoveling (split and alternate), various types of riffler device (e.g., Jones) and mechanical samplers of the Bridgman, Constant, Brunton, and Vezin varieties.

A similar table derived from Reed's calculations is displayed in the Clennell's 'The Cyanide Handbook' (1915), indicating that it had influenced mining sampling for at least 30 years (Fig. 11).



The following table is given for ores of different grades, assuming in all cases that $s = 7$, $l = 1$, and that with samples:

Class A,	m = 50	k = 1	Medium,
" B,	m = 75	k = 10	high-grade,
" C,	m = 500	k = 30	very rich.

TABLE II

Sample Reduced from	Value of D, in Inches		
	Class A	Class B	Class C
100 to 10 tons	5.28	2.96	2.58
10 to 1 ton	2.46	1.38	1.2
2000 to 200 lbs.	1.14	0.6	0.56
200 to 5 "	0.3	0.18	0.16
5 lbs. to 10 assay tons	0.034	0.02	0.018

Figure 11: Table from the 'Cyanide Handbook' following Reed's method and formulae

The last line in this table ("5 lbs. to 10 assay tons") is an *obvious misprint* and should probably read 5 pounds to 10 ounces (oz.).

Clennell had given an earlier table, attributed to Alfred Harvey (Fig. 12), which was published in Mining and Scientific Press Volume LXVIII (88) in January 1904 (Fig. 13).

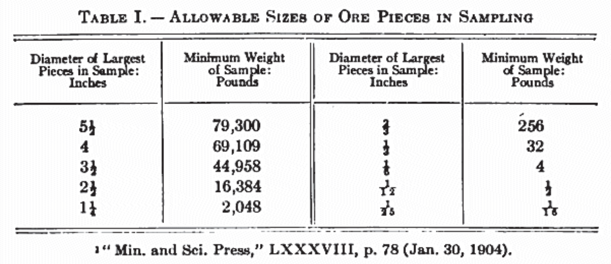
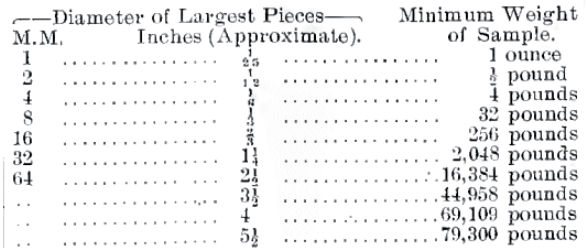


TABLE I. — ALLOWABLE SIZES OF ORE PIECES IN SAMPLING

Diameter of Largest Pieces in Sample: Inches	Minimum Weight of Sample: Pounds	Diameter of Largest Pieces in Sample: Inches	Minimum Weight of Sample: Pounds
5½	79,300	⅔	256
4	69,109	⅓	32
3½	44,958	⅙	4
2½	16,384	1/12	½
1¼	2,048	1/25	1/16

[1] "Min. and Sci. Press," LXXXVIII, p. 78 (Jan. 30, 1904).

Figure 12: Clennell's table (attributed to Harvey) in the 'Cyanide Handbook'



Diameter of Largest Pieces M.M.	Diameter of Largest Pieces Inches (Approximate).	Minimum Weight of Sample.
1	1/25	1 ounce
2	1/12	½ pound
4	⅙	4 pounds
8	⅓	32 pounds
16	⅔	256 pounds
32	1¼	2,048 pounds
64	2½	16,384 pounds
..	3½	44,958 pounds
..	4	69,109 pounds
..	5½	79,300 pounds

Figure 13: Alfred Harvey's Table from MSP Volume 88 1904

Figure 14: March 19, 1926. Orville Wright (far right), chairman of contest committee of National Aeronautic Association, presents the Collier Trophy for 1925 to Dr. S. Albert Reed (second from right), aeronautical engineer, in ceremony at Bolling Field, Washington, D.C. Picture Courtesy of Wright State University Libraries' Special Collections and Archives.

6. Moving into aviation

Reed retired from insurance engineering on October 31st, 1912 (aged 58) and moved into aviation via an attempt to invent a better foghorn. This 'foghorn' turned out to be a route to make an all metal, durable propeller which proved excellent for high-speed applications. There were many wins in the historical Schneider and Pulitzer Trophy events with his design, especially when paired with the Curtiss D-12 engine plus air speed records in the 1920s and 1930s.

All this work led to Reed being awarded the Collier Trophy in 1925, which is awarded annually for "the greatest achievement in aeronautics or astronautics in America, with respect to improving the performance, efficiency, and safety of air or space vehicles, the value of which has been thoroughly demonstrated by actual use during the preceding year" (From Wikipedia).

The Presentation of the Collier Trophy

Dr. S. Albert Reed receiving the Collier Trophy from Orville Wright (right) for the development of the Reed metal propeller

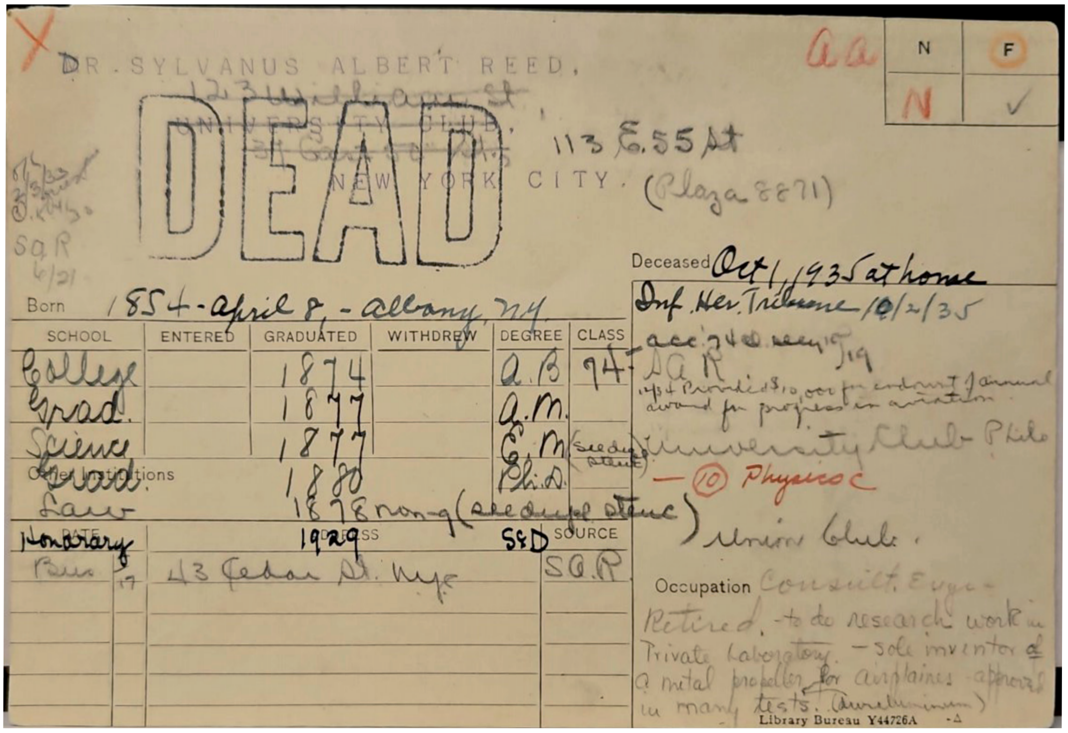
Figure 15: Presentation of the 1925 Collier Trophy to Reed by Orville Wright, Bolling Field, March 19, 1926. From *Aviation* April 19, 1926, Page 605.

7. Legacy

Reed bequeathed to the Institute of the Aeronautical Sciences (IAS) ten thousand dollars ($10000) to endow the "Sylvanus Albert Reed Award". A cash award of the sum of $250 would be awarded annually and Reed himself wrote the first check on Thursday January 30th, 1934. This award (now called the Reed Aeronautics Award) is considered the "highest honor an individual can receive for a notable achievement in aeronautics that represents a significant engineering advancement milestone". The approximate value of $250 USD in 1934 is approximately $6,000 in 2024, and $10000 in 1934 is worth around $250,000 USD today.

Sylvanus Albert Reed died on 1st October 1935 after a "short illness". He is buried with his parents and wife in All Saints Memorial Church Cemetery, Navesink, Monmouth County, New Jersey, USA (Plot: Section 1E, Lot 12).

Below we end this exposé with his Columbia University Alumni Federation card (with the poignant stamp "Dead" on it) that includes an obituary on the right:



X DR. SYLVANUS ALBERT REED.
~~123 William St~~
~~UNIVERSITY CLUB.~~
~~[illegible]~~
113 E. 55 St
NEW YORK CITY. (Plaza 8871)

aa

N	F
N	✓

DEAD

SqR
6/21

Deceased Oct 1, 1935 at home

Born 1854 - April 8, - Albany, N.Y.

SCHOOL	ENTERED	GRADUATED	WITHDREW	DEGREE	CLASS
College		1874		A.B.	74
Grad.		1877		A.M.	
Science		1877		E.M. (see dup. stencil)	
Other Institutions Grad.		1880		Ph.D.	
Law		1878 non-g (see dupl. stenc)			
Honorary		1929		S&D	

DATE		ADDRESS	SOURCE
Bus	17	43 Cedar St. Nyc	SQR

Inf. Her. Tribune 10/2/35
acc. 74 [illegible] 19
SAR
1934 Provided $10,000 for endowment of annual award for progress in aviation.
University Club - Phila
— ⑩ Physics C
Union Club.

Occupation Consult. Engr.
Retired, - to do research work in Private Laboratory. - sole inventor of a metal propeller for airplanes - approved in many tests. (duralumin)

Library Bureau Y44726A

Figure 16: Columbia University Alumni Federation Card "Dead". Courtesy *Columbia University Archives*.

ACKNOWLEDGEMENT

This article has moved on greatly from the material that was first presented as a webinar in 2012 (sadly no longer available). More material has come to light and I in particular would like to thank Jocelyn Wilk of the Columbia University Archives for going the extra mile and digging up excellent pictures of Reed aged 20 in 1874 and 45 in 1899. This article is probably the first time these pictures have seen the literary light of day. I would also like to thank Grace Ethier of Wright State University for tracking down two pictures that appeared in AAHS Journal – pictures of the 1925 Collier Trophy presentation are rarer than hen's teeth, it appears.

References

Biographical material and a description of the Sylvanus Albert Reed Prize are in:

Notes Sylvanus Albert Reed, *Journal of the Aeronautical Sciences Volume 3* Institute 68 – 69 (November 1935).

Sampling:

S. A. Reed (1882). Ore sampling, *The School of Mines Quarterly Volume III*, No. 4, pp. 253 – 260, (May).

S. A. Reed (1885). More remarks on ore Samplin, *The School of Mines Quarterly Volume VI*, No. 4, pp.351- 358, (May).

H. O. Hofman (1899). *The Metallurgy of lead and the desilverization of base bullion, 5th Ed.*, The Scientific Publishing Company. Other editions of this text contain varying amounts of information relating to sampling.

John Edward Clennell (1915). *The Cyanide Handbook 2nd Edition*, McGraw Hill Book Company New York, pp. 385 – 400.

Insurance:

S. Albert Reed (1906). 'The Great Fire in San Francisco: The San Francisco Conflagration of April 1906': special report to the National Board of Fire Underwriters, Committee of Twenty (April.)

Propeller/airscrew material:

S. Albert Reed (1922). Technical Memorandum 168 – Washington (November).

Roger Ward (1958). *The Propeller Pioneer Flying*, December, pp. 30 - 31, 74, 76, 78.

Clearly Roger Ward was at the 1926 dinner dealing with the award of the Collier Trophy in 1925 to S. Albert Reed. As the Flying article was published in 1958, it's likely that Roger was fairly old at this time. It contains many personal reminiscences and details the early history of Reed's interactions with the Curtiss staff at Langley Field.

S. Albert Reed (1928). Technical Development of the Reed Metal Propeller Paper AER-50-25 Presented at the National Meeting of the A.S.M.E. Aeronautic Division, Detroit, MI. June 28 and 29, 1928.

Jeremy R. Kinney (2017). *Reinventing the Propeller*, Cambridge University Press (2017). The salient chapter is Chap. 6 "The Ultimate Solution of Our Propeller Problem" pp. 146 – 179

Terry Gwynn-Jones (1991). *Farther and Faster Aviation's Adventuring Years 1909 – 1939*, Smithsonian Institution Press. Provides details of the air races and competition in the 1920s.

Augmented Scope and Didactics for Initiation to the Theory of Sampling (TOS): Three Domains Behind Valid Data Quality

By Kim H. Esbensen[1]

DOI: 10.62178/sst.003.007

ABSTRACT

Professional comprehension and competence of sampling of particulate and aggregate materials, mixtures, and slurries depend on a minimum set of basic concepts, terms and definitions with derived procedures, equipment design, and practical skills as stipulated in the Theory of Sampling (TOS). Valid analytical data quality assurance involves acknowledgement of three interconnected domains along the lot-to-aliquot-to analysis-to-decision making pathway: i) sampling, ii) analysis, and iii) data analysis/modelling/decision making. This fundamental three-fold domain scope presented here for the first time allows establishment of a new axiomatic 'simplest possible, self-contained' introduction to representative sampling of heterogeneous materials under delineated conditions (TOS).

Introduction - Background

Complete data quality assurance necessitates acknowledgement of three interconnected domains along the full lot-to-aliquot-to analysis-to-decision making pathway: i) sampling, ii) analysis, and iii) data analysis/modelling/decision making. The data analysis/decision making domain is where use of analytical results takes place; this may range from simple data analysis/statistical treatment of analytical data, complex analytical signal calibration (multivariate calibration'), modeling, prediction, and validation to higher level considerations, for example as input to risk assessment. It is counterproductive to view any single, or just two of these three domains in isolation; professional overview is needed for all three.

Professional comprehension and competence of sampling of particulate and aggregate materials, mixtures, and slurries depend on a minimum set of basic concepts, terms and definitions with derived procedures, equipment and practical skills as stipulated in the Theory of Sampling (TOS).

This can be accomplished by comprehension of a set of focus points, constituting the simplest possible' initiation into the complex field of representative sampling:

1. The objective of sampling
2. Physical vs. statistical sampling – a critical distinction
3. All material lots of sampling interest are heterogeneous – the sampling bias
4. Practical sampling follows a universal 'lot-to-aliquot' pathway
5. "Everything" begins in the domain of sampling
6. Theory of Sampling (TOS) at a glance
7. Three necessary-and-sufficient domains behind valid data quality and use of analytical results
8. A new, augmented scope for the Theory of Sampling (TOS)
9. The representative analytical aliquot – the only valid creator of information
10. Error vs. uncertainty – clearing up monumental terminology confusions
11. Global sampling standard, DS 3077:2024 (3rd ed.)
12. Sampling – Historical timeline
13. Full professional competence

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[1] KHE Consulting, Copenhagen, Denmark

This contribution presents a complete three-domain background necessary for fully professional endeavours in the analytical and data analytical domains, amounting to a new, augmented didactic scope for initiation to the Theory of Sampling (TOS); see also [7].

Preamble

The body of concepts, definitions and terms necessary to master a professional competence regarding sampling is not trivial. Despite many claims to the contrary to found in the marketplace or online, for example ‘sampling made simple’ (a hook meant to lure customers to buy sampling equipment and solutions from OEMs on trust) trust us, we are sampling experts’ a.o. But in science, technology, industry, and commerce there are insights and skills that can only be acquired at the expense of a minimum investment of intellectual work. The present new scope for the Theory of Sampling (TOS) intends to provide the holy grail of outreach from the sampling community, i.e., the ‘simplest possible, self-contained’ introduction to sampling of heterogeneous materials and processes under delineated conditions (TOS). This can best be accomplished by gradually developing a set of focus points enabling interested parties (at any level) as well as new practical samplers to acquire the theoretical overview and the practical skills necessary for representative sampling. Below an overview is presented of the theory of sampling as a system’s framework introducing all elements and relationships necessary for full comprehension and practical competence. This article also contains an authoritative glossary of TOS definitions and terms, a curated list of introductions to TOS [1-10], and recommended further in-depth documentation and literature [11-23].

Where and how to start?

How to sample in a manner that will always guarantee a **representative sample**[2] from any lot, be it stationery, or a dynamic moving lot? Enter the **Theory and Practice of Sampling (TOS)**. It is essential to be able to communicate the complex issue of sampling of heterogeneous materials unambiguously, with absolute clarity. This requires a minimum, gradually developing set of definitions and terms.

A very first definition of sampling could be:

Sampling is the process of physical extraction and mass-reduction of a **composite sample** *counteracting* lot/material **heterogeneity** according to conditions as stipulated in the Theory of Sampling (TOS).

Figure 1: Despite lots having infinitely many, widely different manifestations, with infinitely many sizes and grainsize distributions – from TOS’ point of view of they are all but heterogeneous materials with a smaller, intermediate or high degree of heterogeneity (never zero) - which allows them to be sampled with one universal sampling approach: composite sampling.

Credit: KHE Consulting; used with permission.

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[2] Terms in **boldface** are defined in the glossary (Appendix)

Focus #1 – the objective of sampling

The objective of sampling heterogeneous aggregate materials, mixtures, slurries a.o. is to produce a guaranteed **representative analytical aliquot**.

Primary samples are extracted from heterogeneous lots, sub-sampled (where needed in several stages) with the resulting aliquot analysed to estimate one or more properties of interest (quantification of 'the analyte') with which to characterise the lot adequately according to defined objectives e.g., data analytical, statistical, decision-making, business, or regulatory use of analytical results.

A **lot** is characterized by its size (from a miniscule to an extremely large mass) and its inherent material features. A **sample**, S, is a (very) small part of a larger **lot** (L), realized with a sampling rate r = sample weight / lot weight (for example 1:1,000 or 0.1%). While it is no practical challenge to extract a small portion from any lot of any size, using a practical mechanical tool e.g., a spatula, spoon, shovel, spade, corer, cross-stream sampler, mechanical or automated sampler, this is not sampling, only blind bulk mass-reduction. What is needed is **representative sampling**, sampling$_{\text{REPR}}$.

A first set of fundamental terms and definitions includes:

Sampling (verb): a practical, mechanical process (or a virtual equivalent, see **PAT: Process Analytical Technologies**) extracting a physical sample (or intangible representation of a sample in the form of sensor spectroscopic information) from a lot. For the present initiation purpose 'sampling' denotes sampling from a physical lot made up of particulate, aggregate material.

Sample (noun): A portion of a larger lot produced by a documentable representative sampling process under specified conditions.

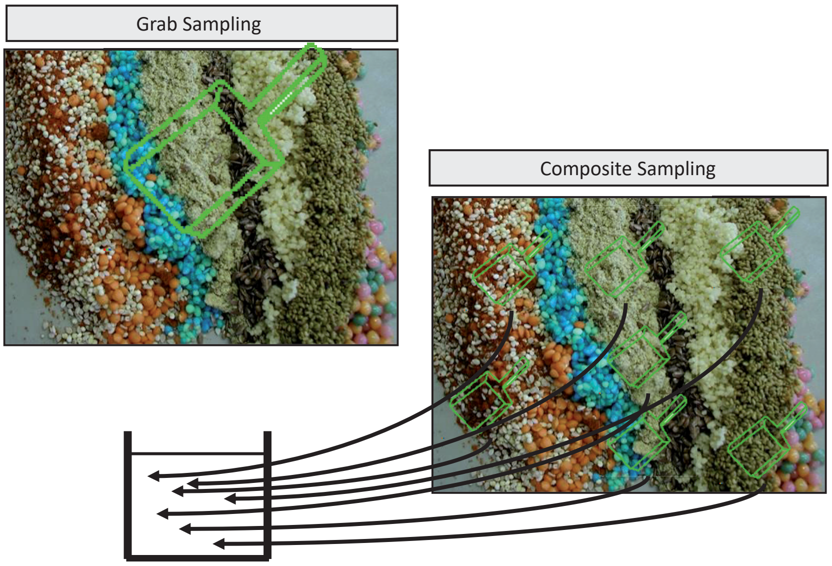
Specimen (noun): Portions extracted from a lot that cannot be documented to result from a representative sampling process are termed **specimens**. Specimens are *worthless* lumps of material because they do not carry valid information regarding their relationship with the original lot; specimens have no useful provenance.

Increment: fundamental unit of practical sampling, defined by a specific mass or volume extracted by a specified procedure using a specific sampling tool.

Grab sampling: process of extracting a *singular* increment. For heterogeneous materials, grab sampling cannot ensure representativity [1-7, 9,11,12].

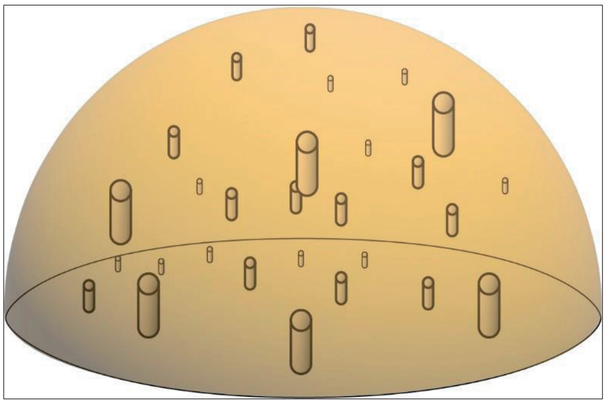
Composite sampling: process resulting in a compound sample made by aggregating a set of Q increments subject to the **Fundamental Sampling Principle (FSP)**. Q can be focused to make sampling *fit-for-purpose*.

Representativity (noun): prime objective of all proper sampling processes. Representativity refers to intrinsic material features, e.g., composition, grain size distribution, physical properties (e.g., intrinsic moisture). The representativity status of an individual sample cannot be defined nor ascertained if removed from the context of its generating sampling-and-analysis pathway. The attribute 'representative' can only be accorded a sampling process in compliance with all relevant demands specified by TOS.



Credit: KHE Consulting; used with permission.

Figure 2: Grab sampling vs. **composite sampling**



Credit: KHE Consulting; used with permission.

Figure 3: Fundamental Sampling Principle (FSP)

Fundamental Sampling Principle (FSP): mandated principle for sampling processes ensuring all increments an identical, non-zero extraction probability while covering the full material lot (volume/mass). Sampling of a lot in which certain areas, volumes, parts are not physically accessible cannot ensure representativity.

Process Analytical Technologies (PAT): Sampling performed using a suitable sensor technology allowing acquisition of spectral characterization of a delineated volume of a ducted flux of matter (a 'process sample') by way of an appropriate sampling interface [22]. In the realm of process sampling, PAT is aka 'sensor sampling'.

Focus #2: physical vs. statistical sampling – a critical distinction

It is essential to distinguish between:

Sampling (*from a physical lot*), sampling$_{TOS}$

versus

Statistical sampling (*from a population of units*), sampling$_{STAT}$

Long lasting terminology ambiguity between sampling$_{TOS}$ and sampling$_{STAT}$ has caused significant confusion across and between many scientific disciplines and technological/ industrial application fields, see [8,9] for in-depth treatment. This distraction can first be fully resolved after all terms and definitions pertaining to TOS have been properly comprehended. For the present initiation purpose sampling shall always denote sampling$_{TOS}$ unless otherwise specified.

Focus #3: All material lots are heterogeneous – the sampling bias

Heterogeneity is one of two key influential factors that must be counteracted by all practical sampling processes, lest these will be compromised by a fatal **sampling bias**. A sampling bias will also be incurred by an incorrect[3] sampling procedure, e.g., **grab sampling**. A sampling bias is fundamentally different from an analytical bias. While the latter can be subjected to a conventional analytical laboratory bias-correction, the sampling bias cannot be corrected by any means (data analytical, statistical, other). Instead, TOS stipulates that all sampling operations must be designed to eliminate the so-called Incorrect Sampling Errors (ISE), which, when unmitigated, are unavoidable hidden sampling bias generators, see Focus #6 and [1-10].

Focus #4: Universal sampling$_{TOS}$ 'lot-to-aliquot' pathway

"What is the meaning of analysing, with ultimate analytical accuracy and precision, the concentration of an **aliquot** that represents only a *miniscule* 1/10^3 - 1/10^9 mass-reduced fraction of the original lot mass - if the process by which it is obtained is compromised, not representative?" None, there is no meaning! The resulting analytical results carry no reliable information about the original lot. Non-representative samples, sub-samples and aliquots unavoidably lead to non-representative analytical results, *regardless* of the quality of analysis. All costs incurred in sampling 'from-lot-to-aliquot-to-analysis' are therefore lost and cannot ever be recouped. Therefore, focus must be exclusively on *how* to guarantee extraction of representative primary samples, followed (equally important) by a number of representative mass-reducing sub-sampling stages [6,12] until having produced the representative aliquot – to be delivered to the domain of analysis.

Focus #5: "Everything" begins in the domain of sampling

It is necessary to step back from the traditional preoccupation with analytical accuracy, analytical precision, which resides in the domain of analysis to the 'before analysis' domain. This is the sampling domain (*verb*) – not the sample (*noun*) domain. The latter designation would imply that 'samples' are already existing, ready to be selected and extracted *in toto*. However, the reality concerning how to sample heterogeneous materials, lots and processes is very different.

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[3] Incorrect vs. correct sampling errors a.o., see Focus #6 and references [1-10]

Representative sampling must follow the universal pathway ‘from-lot-to-aliquot’ that demands appropriate scientific and technological competence, enter the **Theory of Sampling (TOS)**. Everything is critically dependent upon the competence and skills needed for the extraction of a representative primary sample from the lot (regardless of the world’s very many, very different lot manifestations).

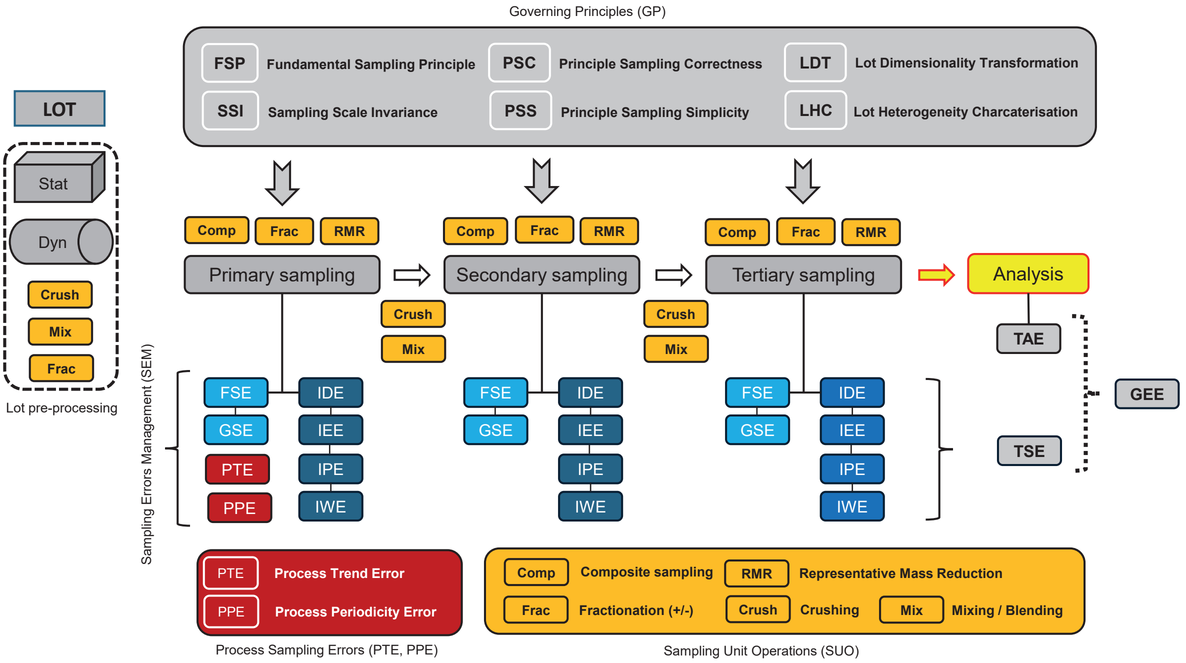
Presciently TOS makes provisions allowing for a *unified* approach, Fig. 4. By focusing on the *common* characteristics of material heterogeneity [1-7,11], it is possible to address sampling of all types of material using a singular *generic* sampling pathway, governed by the principles and unit operations in the Theory of Sampling (TOS). This is perhaps the most enabling aspect of TOS: Since all materials are heterogeneous (it is only a matter to which degree large, intermediate, small, but never zero), TOS’ generic sampling pathway is universally applicable to *all* types of material, appearing with *any* lot size, under *all* specified conditions. As one example, TOS applies with equal force for *any* primary size lot, but *also* in all the world’s analytical laboratories for *all* menial sub-sampling operations needed here; it is only the *scale* differs (Principle of Sampling Scale-Invariance).

Focus #6: Theory of Sampling (TOS) - everything at a glance

The ultimate purpose of the use - and the scientific, regulatory, technological, or economic value of analytical results are all dependent on the imperative demand for all analytical aliquots to be *representative* of the *original heterogeneous lot/material* in question.

The sampling-to-analysis pathway is always a **multi-step process**, starting with primary sampling of the lot, ending with analysis of the aliquot (or test portion). This process always involves significant mass reductions with typical sampling rates (m/m) $1{:}10^3$ to $1{:}10^9$: lot (~tons) → primary samples (~kilograms) → secondary samples (~grams) → analytical aliquot (grams to micro grams) → analytical measurement. This is all required to be conducted in such a way that the final analytical result *represents* the salient properties of the original lot in an objectively documentable, fully reliable way [7].

The **Theory of Sampling (TOS)** is the only complete science-backed framework defining its role to be the guarantor of both **sampling accuracy** w.r.t., the original lot, and of **sampling precision** w.r.t., *reproducibility of the analytical aliquot*. Until physical delivery of the aliquot for analysis, this responsibility exclusively resides in the sampling domain. While the specific nature of ‘the analyte’ may imply various constraints (the analyte may for example be a physical characteristic of the sampled material, e.g., compression strength of concrete), this has no principal impact on how to conduct the *preceding* multi-stage sampling and sub-sampling process(es), which all takes place before analysis.



Credit: KHE Consulting; used with permission.

Figure 4: Theory of Sampling (TOS) Principal system’s framework DS 3077: 2024 (3rd ed) [7].

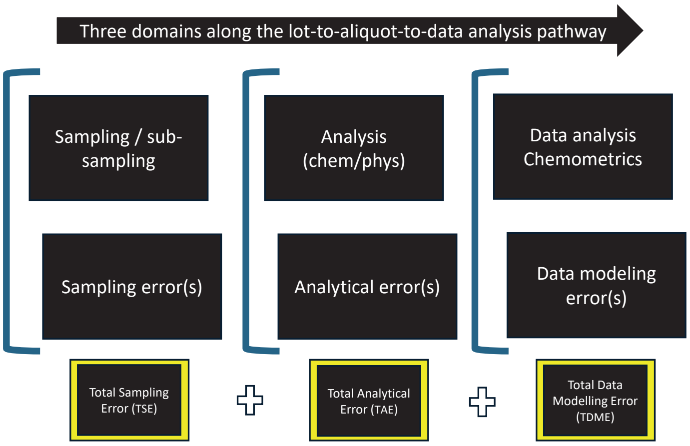
Focus #7: Three principal domains – necessary for optimal data quality

Complete quality assurance of analytical data necessitates acknowledgement of three fundamental *domains* along the full 'lot-to-aliquot-to analysis-to-decision making' pathway, which are:

1. The 'before analysis' domain (the sampling and sub-sampling domain)
2. The domain of analysis *s.s.*
3. The DSR domain (Data analysis; Statistics; Risk management; decision making).

The DSR domain is where the use of *analytical results* takes place, ranging from simple data analytical/statistical data treatment, via complex analytical signal calibration (chemometric multivariate calibration), modeling, prediction and validation), to higher level decision-making considerations, for example, as input to risk assessment [17].

It is counterproductive to view any single, or just two of these three domains in isolation. The feature 'data quality' has all too long been viewed as only related to analytical uncertainty, with seriously detrimental effects since leaving out all sampling uncertainty – and sometimes also ignoring errors and uncertainty effects associated with DSR operations on analytical data. Reliable use of quantitative 'data' must be based on acknowledgement of all three interconnected domains making up the full 'lot-to-aliquot-to-analysis-to-DSR' pathway.



Credit: KHE Consulting; used with permission.

Figure 5: Three successive domains are involved to cover the full 'lot-to-analysis-to-DSR' pathway.

Each domain is characterized by potential errors (TSE), (TAE), (TDSRE), which give rise to *uncertainty* effects (Focus #10).

It is the responsibility of specific domain expertise to minimize, or eliminate (where possible), all domain errors and effects (uncertainties). If no counteracting measures are taken, the 'before analysis' sampling domain will very nearly always dominate the total uncertainty budget: $MU_{total} = MU_{sampling} + MU_{analysis} + MU_{DSR}$.

In this context, from a logical, scientific and economic point of view all efforts and costs spent on analysis of what in reality are **specimens** is futile. The actions taking place in subsequent domains, i.e., data analysis/data modelling/statistical or critical decision-making domains, or regarding **Risk Management (RM)** will be seriously affected, with data quality unavoidably compromised. There is a ticking time bomb embedded in data for which the demands for *data quality* have not been adequately defined *before* sampling and analysis. Non-representative sampling is (like) the original sin: sampling error effects are passed on to the subsequent domains in the lot-to-analysis-to-DSR pathway in the form of hidden, uncontrollable additions to the total Measurement Uncertainty (MU_{total}) which will always be inflated to a degree larger than necessary. But there is no way to estimate the magnitude of such excess uncertainty incurred - and data quality issues cannot be rectified in any way in the post-analysis domain (sampling domain *corrections* are not possible). Data quality originates in, and must be optimized, starting with the sampling domain.

Perhaps the most prominent example of the need for complete domain comprehension concerns **Process Analytical Technologies (PAT)**, an approach for process sampling using appropriate sensor technologies to acquire spectral information from a delineated target volume in front of a sensor followed by powerful *multivariate calibration* (chemometrics) a.o.[3] But the PAT approach is overwhelmingly only concerned with the challenging analytical aspects together with the subsequent domain. PAT is an essential element of process monitoring and control, which are part of the DSR domain, all the while leaving the sampling domain overlooked. This has serious, often fatal consequences, as the delineated analytical volume is very nearly always just a minute fraction of the cross-section of the flowing stream resulting in a serious **sampling bias**. Very many current PAT solutions are flawed in this respect; full details can be found in [9,22].

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[3] This discipline is treated in full in SST#4, which is devoted to the theme Process Analytical Technology (PAT) vs. Process sampling.

Focus #8: A new, augmented scope for the Theory of Sampling (TOS)

From this three-domain context emerges a new paradigm regarding accuracy and precision in relation to sampling and analysis of heterogeneous lots/materials. It is critical that the full lot-to-aliquot is front and center:

Analytical accuracy and *analytical* precision, $MU_{analysis}$, *only* characterises the specific analytical method employed, thereby *missing* the dominating MU contributions stemming from sampling, $MU_{sampling}$. Users of analytical results cannot make valid and reliable decisions without information about *both* uncertainty contributions and should therefore always be supplied with information regarding MU_{total}, the *effective* total uncertainty. To this must be added the MU_{DSR} as appropriate to the situation.

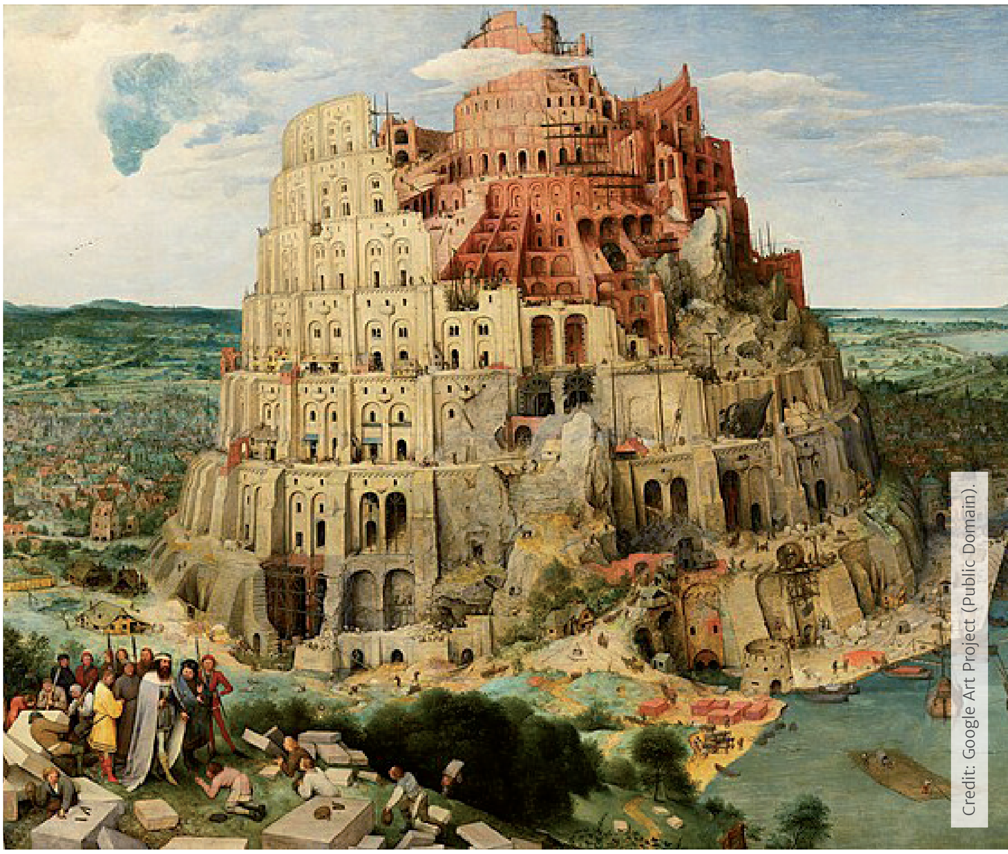
Credit: Google Art Project (Public Domain).

Figure 6: "Tower of Babel" by Pieter Bruegel the Elder (1563)

Focus #9: The analytical aliquot – only valid *creator* of relevant information

In the three-domain context, the analytical aliquot is the *physical manifestation* of translating from the domain of sampling to the domain of analysis. The *quality* of an aliquot is not related to the aliquot itself (which may come as a surprise to many) but is *exclusively* a function of the *sampling process* by which is was produced. In this context, the aliquot (strictly speaking, analysis of the aliquot) is the only valid creator of information about the original lot (stationary or moving). Also, it is not possible to ascertain whether a specific sample or aliquot is representative, or not, from any considerations only relating to the sample/sub-sample/ aliquot itself. Therefore, focus shall *exclusively* be on the *sampling process*, which must be fully TOS-compliant for the aliquot to be *documentable* as representative [1-10]. Also, there is no declination of the attribute 'representative'. A sampling process, or a resulting sample either <u>is</u> or is <u>not</u> representative.

Focus #10: Error vs uncertainty

There unfortunately exist scores of fundamentally *different* definitions of the concepts and terms *error* vs. *uncertainty* in various scientific disciplines, educational traditions and related literatures, often severely at odds with one another. The relationship between these is well likened to the Tower of Babel as has been extensively presented and debated in [8,9].

There is only one scientific way out of this quagmire: Clear, unambiguous definitions are mandatory as part of all outreach and educational endeavours. It is essential that analytical results are always reported *together* with a realistic total estimate of the associated Measurement Uncertainty, $MU_{total} = MU_{sampling} + MU_{analysis} + MU_{DSR}$. Currently, the uncertainty contribution from sampling is overlooked all too often with highly detrimental consequences because $MU_{sampling}$ can be 10-25-50 times *larger* than $MU_{analysis}$ depending on the level of sampling errors effects incurred by ignoring, or not being aware of, the critical adverse heterogeneity influence on the sampling process. An in-depth discussion of this status quo, with a critical focus for the DSRM domain, is presented in [9].

Focus #11: Global sampling standard DS 3077:2024 (3rd ed)

2024 saw publication of the 3rd revision of the standard DS 3077:2024 "Representative Sampling – Horisontal Standard" [7]. A succinct summary is as follows:

> "The theory of sampling is a generic, matrix-independent framework for representative sampling of all types of aggregate and mixture materials (solid, slurries) in all grain-size brackets (from broken ores to powders). The universal sampling principles can be applied uniformly to all types of materials, and lots composed by aggregate particular matter and slurries (gasses and liquids are not covered by this document). This document describes a generic sampling process in sufficient detail and covers all elements necessary and sufficient for the stated objective enabling documentation of sampling representativity under the specified conditions for the sampling process employed. This document is based on the theory of sampling (TOS), constituting a complete competence basis for representative sampling, and ensuring appropriate levels of accuracy and precision for both primary sampling as well as for all subsampling procedures and mass-reduction systems at the subsequent laboratory stages before analysis…" [7, p.8]

This universal standard for representative sampling is aimed at all individuals with vested interest and/or responsibility for sampling (technical and supervisory personal, managers, stakeholders, companies, corporations, organisations and other relevant *legal persons*). The present compact initiation can be viewed as the 'simplest possible, self-contained introduction' for all of these agents (including legal and accounting departments).

All educational introductions are complemented by the following *call-to-action* [4,9], Fig. 7.

All sampling procedures invoked to secure primary samples, and all sub-sampling operations used to produce the final analytical aliquot, shall be compliant with the principles of representative sampling as stipulated by the Theory of Sampling (TOS).

All sampling procedures shall be adequately and fully documented, see DS 3077:2024 (3.ed.)

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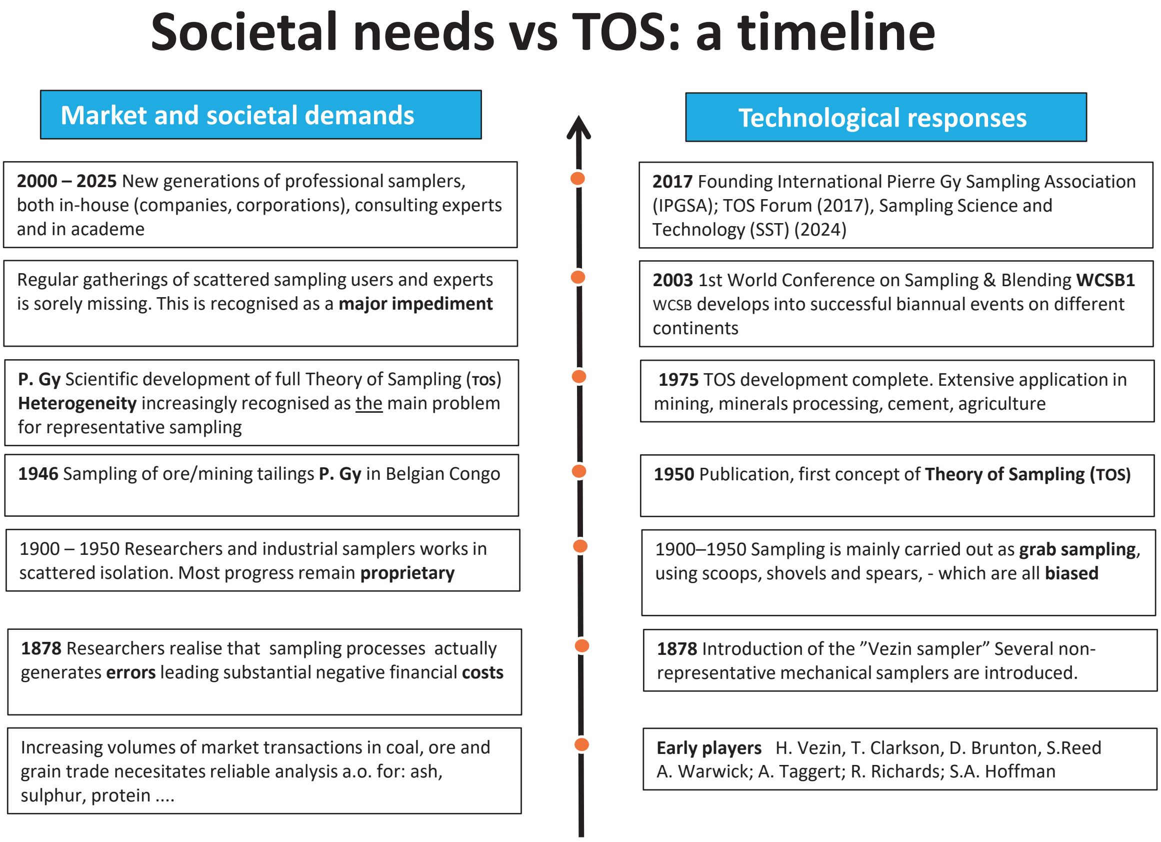
Figure 7: Proposal for a universal creed for responsible representative sampling, the Theory of Sampling (TOS) [7]

Henceforth, it is proposed to include these two statements wherever relevant in every commercial and trade contract and in any other guidance documentation that is based on, or includes sampling. This will reduce a substantial proportion of legal disputes stemming from isolated comparison of analytical results without the necessary three-domain recognition. In-depth treatment of this "assay exchange" issue can be found in [10], where it is shown that most, if not all such disputes simply reflect a lack of proper TOS understanding and competence. For the present initiation to TOS, a Glossary can be found in the Appendix. A broader selection of definitions and terms can be found in [7].

Focus #12: A historical timeline

Figure 8 presents a brief historical timeline of ca. 150 years of development of market needs/demands in societal sectors where early attempts at 'sampling' gradually emerged as first technological solutions. This development was fragmented and scattered until 1950, the year of a publication containing the first recorded vestiges of what came to be the Theory of Sampling (TOS) later on (in 1975). It took 25 more years until organised activities saw the light of day (2003) in the form of the 1st World Conference on Sampling and Blending (WCSB1), the founding of the International Pierre Gy Sampling Association (IPGSA) in 2017, and the start and continuation of dedicated publication activities: TOS-Forum, Sampling Science and Technology (2017-present). Two accounts of this development can be found in [22,23]. The International Pierre Gy Sampling Society (IPGSA) launched a fully updated homepage in 2025.



Societal needs vs TOS: a timeline

Market and societal demands	Technological responses
2000 – 2025 New generations of professional samplers, both in-house (companies, corporations), consulting experts and in academe	**2017** Founding International Pierre Gy Sampling Association (IPGSA); TOS Forum (2017), Sampling Science and Technology (SST) (2024)
Regular gatherings of scattered sampling users and experts is sorely missing. This is recognised as a **major impediment**	**2003** 1st World Conference on Sampling & Blending **WCSB1** WCSB develops into successful biannual events on different continents
P. Gy Scientific development of full Theory of Sampling (TOS) **Heterogeneity** increasingly recognised as the main problem for representative sampling	**1975** TOS development complete. Extensive application in mining, minerals processing, cement, agriculture
1946 Sampling of ore/mining tailings **P. Gy** in Belgian Congo	**1950** Publication, first concept of **Theory of Sampling (TOS)**
1900 – 1950 Researchers and industrial samplers works in scattered isolation. Most progress remain **proprietary**	1900–1950 Sampling is mainly carried out as **grab sampling**, using scoops, shovels and spears, - which are all **biased**
1878 Researchers realise that sampling processes actually generates **errors** leading substantial negative financial **costs**	**1878** Introduction of the ”Vezin sampler” Several non-representative mechanical samplers are introduced.
Increasing volumes of market transactions in coal, ore and grain trade necesitates reliable analysis a.o. for: ash, sulphur, protein	**Early players** H. Vezin, T. Clarkson, D. Brunton, S.Reed A. Warwick; A. Taggert; R. Richards; S.A. Hoffman

Figure 8: Timeline of development of sampling (practice and theory) as solutions to developing market and societal needs/demands in the last ~150 years.

Focus #13: Full professional competence

References [1-9] present a curated collection of general introductory literature on the Theory and Practice of Sampling (TOS) at entry level, [10-22] adding to this curriculum with accounts of applied TOS from selected scientific, technological and industrial application fields.

For guided competence building, TOS recommends the following reading order:

- Tier 1 (introductory): [1,2,7,8,6,12,11,21]
- Tier 2 (more advanced learning): [9, 4,3,5,17] [10,13-16,18-20, 22]

Selected contributions on the history of the theory and practice of sampling can be found in [23-24].

References

1. Esbensen, K.H. & Wagner, C. (2014). Why we need the Theory of Sampling, *The Analytical Scientist*, 21 (Oct.), pp. 30-38.

2. Esbensen, K.H. (2024). *Introduction to the Theory and Practice of Sampling*. p. 328, SIX-P Publishing, Wedel, DE.

3. Pitard, F.F. (2019). *Theory of Sampling and Sampling Practice*, 3rd ed., CRC Press, Boca Raton, Florida. p. 665. ISBN 978-1-1138-47648-6

4. Gy, P. (1998). *Sampling for Analytical Purposes*, Elsevier, Amsterdam, NE., p. 148. ISBN 0-471-97956-2

5. Lyman, G. J. (2020). *Theory and Practice of Particulate Sampling Theory – an Engineering Approach*. Materials Sampling & Consulting, Brisbane, Queensland, AUS. Geoff Lyman - Owner - Materials Sampling & Consulting Pty Ltd | LinkedIn

6. Petersen, L., Dahl, C., & Esbensen, K.H. (2004). Representative mass reduction in sampling – a critical survey of techniques and hardware. in Special Issue: 50 years of Pierre Gy's Theory of Sampling, In K.H. Esbensen & P. Minkkinen (Eds.), Proceedings of the First World Conference on Sampling and Blending (WCSB1), Esbjerg, DK., *Chemometrics and Intelligent Laboratory Systems*, 74(1), pp. 95-114.

7. DS 3077 (2024). *Representative Sampling— Horizontal Standard* (3rd ed.). Danish Standards, Fonden Dansk Standard, Nordhavn, Copenhagen, DK. https://webshop.ds.dk/en/standard/M374267/ds-3077-2024

8. Esbensen, K.H. & Pitard, F.F. (2022). Errors vs uncertainty vs measurement uncertainty. *Spectroscopy Europe/World, 34*(6/7).

9. Esbensen, K.H. (forthcoming 2025). Data Quality: Importance of the 'before analysis' domain (Theory of Sampling, TOS). *Journal of Chemometrics*. Special Issue "Tribute to Paul Geladi".

10. Esbensen K.H. & Vogel A.D. (2023). Unsubstantiated complacency re. the "assay exchange" paradigm: sampling uncertainties with hidden economic consequences. *ALCHEMIST 110* (July), pp. 14-21.

11a. Esbensen, K.H., Paoletti, C. & Theix, N. (2015). (Eds.) Journal AOAC International, Special Guest Editor Section (SGE): *Sampling for Food and Feed Materials*. pp. 249-320.

11b. Esbensen, K. H. (2015). Journal of AOAC International (JAOAC) Special Issue on Representative Sampling for Food and Feed Materials: A Critical Need for Food/Feed Safety. *TOS forum, 4*, p. 12. https://doi.org/10.1255/tosf.39

12. Petersen, L., Minkkinen, P. & Esbensen, K.H. (2005). Representative Sampling for reliable data analysis: Theory of Sampling, *Chemometrics and intelligent laboratory systems*, 77(1-2), pp. 261-277.

13. Esbensen, K. H., Romañach, R. J. & Román-Ospino, A. D. (2018). Theory of Sampling (TOS): A Necessary and Sufficient Guarantee for Reliable Multivariate Data Analysis, Chap. 4 in Ferreira, A. P., Menezes, J. C.; Tobyn, M. (Eds.), *Pharmaceutical Manufacturing in Multivariate Analysis in the Pharmaceutical Industry*, pp. 53-91. Academic Press, ISBN 978-0-12-811065-2

14. Esbensen, K.H., Paoletti, C. & Minkkinen, P. (2012). Representative sampling of large kernel lots – I. Theory of Sampling and variographic analysis, *Trends in Analytical Chemistry (TrAC), 32*, pp.154-165, doi:10.1016/j. trac.2011.09.008

15. Minkkinen, P., Esbensen, K.H., & Paoletti, C. (2012). Representative sampling of large kernel lots – II. Application to soybean sampling for GMO control. *Trends in Analytical Chemistry (TrAC), 32*, pp. 166-178, doi:10.1016/j.trac.2011.12.001 170.

16. Esbensen, K.H., Paoletti, C. & Minkkinen, P. (2012). Representative sampling of large kernel lots – III. General Considerations on sampling heterogeneous foods, *Trends in Analytical Chemistry (TrAC), 32*, pp. 179-184, doi:10.1016/j.trac.2011.12.002

17. Paoletti, C. & Esbensen, K.H. (2022). Framing TOS in risk assessment: an outreach perspective for the future, in *Proceedings of WCSB10. TOS Forum Issue 11*, pp. 419–423

18. Esbensen, K.H. & Abu-Khalaf N. (2022). Before reliable near infrared spectroscopic analysis - the critical sampling proviso. Part 1: Generalised theory of sampling, *Journal of Near Infrared Spectroscopy 30*(6), pp. 291-310, doi:10.1177/09670335221124612

19. Esbensen, K.H. & Abu-Khalaf N. (2022). Before reliable near infrared spectroscopic analysis- the critical sampling proviso. Part 2: Particular requirements for near infrared spectroscopy, *Journal of Near Infrared Spectroscopy. 30*(6), pp. 311-321, doi:10.1177/09670335221124611

20. Esbensen, K. H. & Romañach, R. J., (2020). Sampling for NIR-analysis. Chap. 19, in *Handbook of NearInfrared Analysis*, 4th Ed. Ciurczak, E.W., Igne,B., Workman,J., Burns, D.A. (Eds.) CRC Press, Taylor & Francis Group. ISBN: 978-1-138-57648- 3

21. Abel Arkenbout, Stéphane Brochot, Trevor Bruce, Pedro Carrasco, Pablo Carrasco, Philippe Davin, Quentin Dehaine, Oscar Dominguez, Simon C. Dominy, Kim H. Esbensen, Dominique François-Bongarçon, Melissa Gouws, Ralph J. Holmes, Li Huachang, Eduardo Jara, Martin Lischka, Geoff Lyman, Zhu Mingwei, Pentti Minkkinen, Richard C.A. Minnitt, Claudia Paoletti, Christopher Robben, Rodolfo J. Romañach, Elke Thisted & D. Aldwin Vogel (2021). *Economic arguments for representative sampling. Spectroscopy Europe/World*, *33*: 7, https://wcsb10.com/media/0gzbw012/wcsb10-economic-arguments-dec-2022-compressed.pdf

22. Esbensen. K.H. & Sivalingam, V. (2020). The sampling interface—A critical Theory of Sampling success factor in process sampling and PAT. *Proceedings of WCSB10: TOS Forum Issue 11*, pp. 115–129

23. Esbensen, K.H. (2004). "50 years of Pierre Gys 'Theory of Sampling'– a tribute", in Special Issue Proceedings: *First World Conference on Sampling and Blending (WCSB1)*. K.H. Esbensen & P. Minkkinen (Eds). *Chemometrics and Intelligent Laboratory Systems*, vol. 74, Issue 1, p. 3-6

24. Minnitt, R.C.A. & Esbensen, K.H. (2017). Pierre Gy's development of the Theory of Sampling: a retrospective summary with a didactic tutorial on quantitative sampling of one-dimensional lots. *TOS Forum* 7, pp. 7-19. doi: 10.1255/tosf.96

Appendix: Glossary

Lot: specified target material to be subjected to a specified sampling procedure. The term lot refers both to the material as well as to size (volume/mass), physical characteristics and geometric form. Lots are distinguished as *stationary* or *dynamic* (moving lots). A dynamic lot is a material stream where sampling is carried out at a fixed location. For both stationary and dynamic lots, sampling procedures must address the entire lot volume guided by the Fundamental Sampling Principle (FSP).

Mass-reduction: divisionary process leading to one or more *sub-samples* (portions) [m/m] of a larger lot/sample/sub-sample, with the objective of being representative of the original lot.

Sampling: (sampling procedure; sampling process): grab sampling or composite sampling.

Increment: fundamental unit of practical sampling, defined by a specific mass or volume extracted by a specified sampling tool.

Grab sampling: process of extracting a singular increment. Grab sampling cannot ensure representativity for heterogeneous materials.

Composite sampling: process leading to a compound sample (composite sample) made by aggregating a set of Q increments subject to the Fundamental Sampling Principle (FSP). Q can be set to make sampling fit-for-purpose according to a specific criterion.

Sample: extracted portion of a lot that can be documented to be a result of a representative sampling procedure (non-representatively extracted portions of a lot are termed specimens).

Sampling accuracy: Closeness of the analytical result of an aliquot w.r.t., to the true concentration of a lot. NB. Sampling accuracy always includes the analytical imprecision, since analysis is always based on an analytical aliquot, which is the end result of a complete 'lot-to-aliquot' sampling pathway. Therefore: "sampling accuracy" = "sampling + analytical accuracy".

Sampling precision: Variance of the series of analytical determinations in a Replication Experiment (RE). NB. Sampling precision always includes the analytical precision, since all analysis is always based on an analytical aliquot, which is the end result of a complete 'lot-to-aliquot' sampling pathway. Therefore, "sampling precision" = "sampling + analysis precision".

Analytical precision: Variance of repeated analytical determinations made on one-and-the-same aliquot. Analytical precision is *only* a characteristic of the analytical method.

Analytical accuracy: Deviation between the average of a series of repeated analytical determinations on one-and-the-same aliquot and the true average concentration of a lot. Analytical accuracy is *only* a characteristic of the analytical method.

Specimen: portion of a larger mass/volume extracted by a non-representative sampling process.

Fundamental Sampling Principle (FSP): principle governing a sampling process ensuring all increments an identical, non-zero extraction probability while covering the entire material lot (volume/mass). Sampling of a lot in which certain areas, volumes, or parts are not physically accessible cannot ensure representativity.

Fit-for-purpose representativeness: characteristic of a sampling process in which the Total Sampling Error (TSE) has been reduced to below a predefined threshold level.

Sampling bias: Difference between true lot concentration and grab sample or composite sample concentration determination (or average of replicate sample concentration determinations), whether sampled representatively or not.

Compositional heterogeneity (CH): compositional differences between *individual* fundamental units of a material (grains, particles, fragments). CH is an intrinsic characteristic of the target material to be sampled.

Distributional heterogeneity (DH): compositional differences between *groups* of fundamental units of a target material. Groups of units manifest themselves as practical increments used in sampling. DH is an expression of the spatial heterogeneity of a material to be sampled.

Grain-size heterogeneity (GH): compositional difference due to assemblages of units with different grain-size.

Lot heterogeneity: CH + DH + GH

Homogeneity: an assemblage of material units with *identical* unit size, composition, surface characteristics a.o. N.B. there are practically no homogenous materials in the realm of technology, industry, commerce a.o. of interest for sampling. All materials from these realms are in practice heterogeneous.

Representativity: prime objective of all sampling processes. Representativity refers to intrinsic material features, e.g., composition, grain size distribution, physical properties (e.g., intrinsic moisture). The representativity status of an individual sample cannot be defined, nor ascertained in isolation. i.e., if removed from the context of its full sampling-and-analysis pathway. The characteristic representative can only be accorded a sampling process in compliance with all relevant demands specified by TOS [1-10]. NB: For full mathematical-statistical definition see [3,4,5].

Theory of Sampling (TOS) (Theory and Practice of Sampling): necessary-and-sufficient framework of governing principles (GP), sampling unit operations (SUO), sampling error management rules (SEM) together with derived practices and skills needed to overcome adverse effects of material heterogeneity and non-representative sampling procedures.

Aliquot (analytical aliquot): ultimate sub-sample extracted in a 'lot-to-aliquot' pathway intended for analysis – or a *virtual* sample, e.g., a delineated volume of a stream of matter interacting with a spectroscopic analytical instrument (in the realm of Process Analytical Technologies, PAT).

Measurement Uncertainty (MU): (metrological term): MU expresses the variability interval of values attributed to a quantity measured. MU is the effect of a particular error, e.g. a sampling error, an analytical error or a data modelling error a.o. – or of combined effects (see MU_{total}).

- $MU_{sampling}$ reflects the variability stemming from sampling uncertainty
- $MU_{analysis}$ reflects the variability stemming from analytical uncertainty
- MU_{total} is the effective uncertainty stemming from both sampling and analysis
- $MU_{total} = MU_{sampling} + MU_{analysis} + MU_{DSR}$

Precision: Statistical variance $(STD)^2$. In practical sampling and analysis contexts 'precision' is a measure of imprecision.

Replication Experiment (RE): Replication of a series of independent complete 'lot-to-aliquot' analytical determinations, made under identical conditions. The number of replications is termed Q.

Total Sampling Error (TSE): TSE is causing the combined uncertainty effects resulting from material extraction along the full sampling pathway from-lot-to-aliquot.

Total Analytical Error (TAE): TAE is causing the combined uncertainty effects specifically resulting from analysis of the aliquot only.

Total Data modelling, Statistics, Risk management Error (TDSRE): TDSRE is causing the combined uncertainty effects resulting from post-analysis data treatment (DSR).

Stakeholder: legal person (company, corporation, agency or individual) with a vested interest or concern. Process Analytical Technologies (PAT): In the current process industry arena, analytical endeavors are increasingly sought to be served by the Process Analytical Technology (PAT) framework, offering a plentitude of on-line, mostly spectroscopic analytics: UV-VIS, NIR, RAMAN, NMR, ‘acoustic chemometrics’ a.o. See [12] as an introduction.

Sampling manager: legal person to whom responsibility is given for all actions related to sampling in a specified scientific, technological, industrial, business or other context.

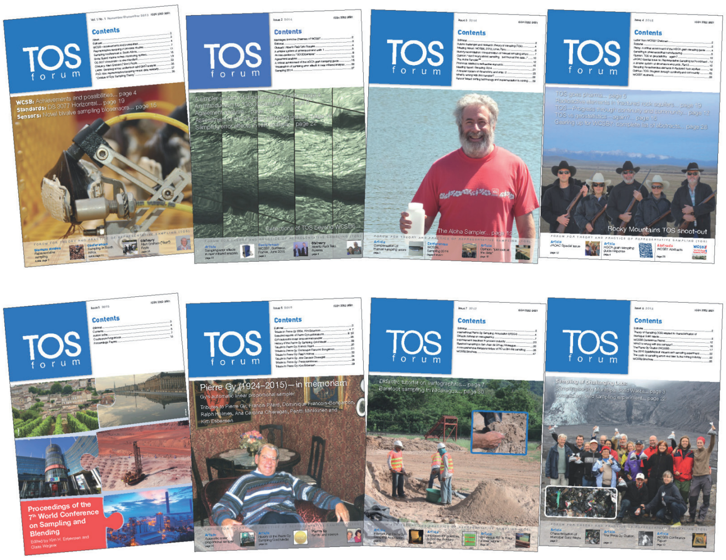
Legal person: a legal person is any person or other legal entity that can do the things a human person is usually able to do in law – such as enter into contracts, commit to specified obligations and responsibilities.

TOS forum

Starting 2024 *Sampling Science and Technology* (SST) is a direct continuation of *TOS forum*, which was published by IMPublications in the decade 2013-2023.

The complete archive can be found here:

sst-magazine.info/tos-forum

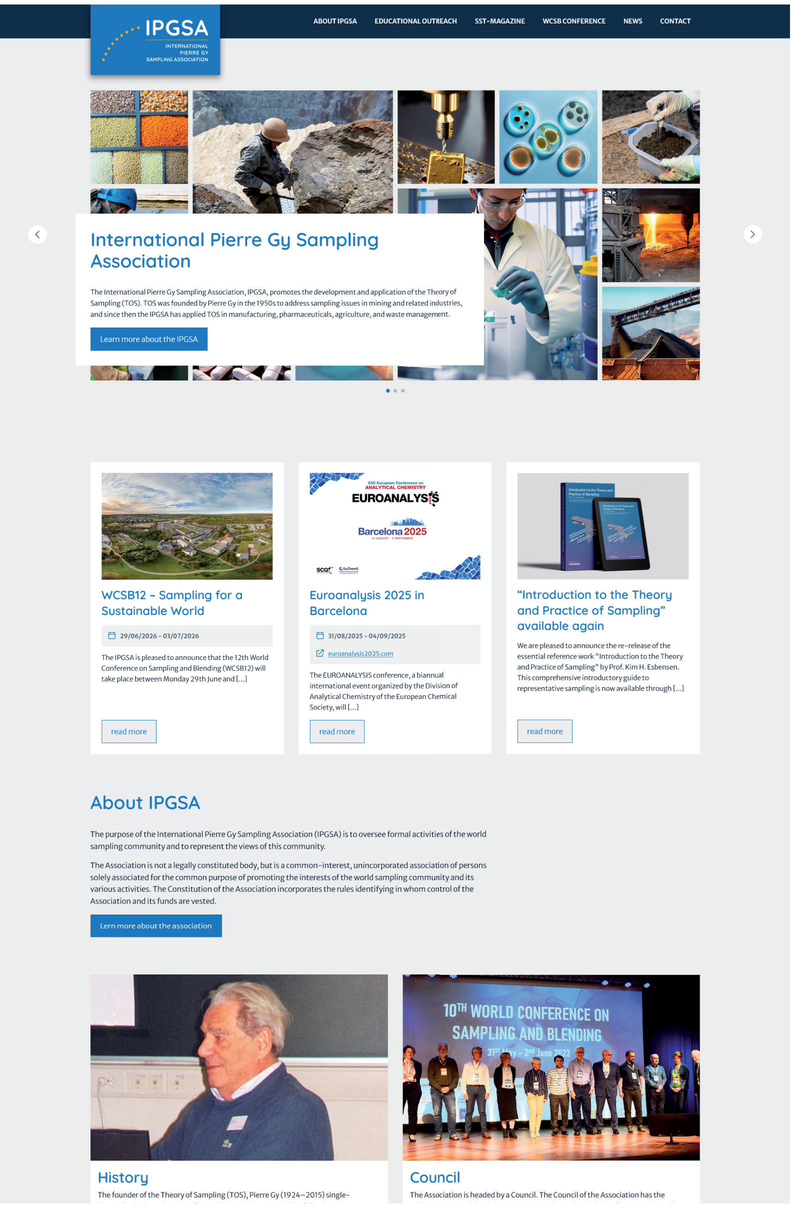


Launch of the New Website of the International Pierre Gy Sampling Association (IPGSA)

By Martin Lischka[1]

DOI: 10.62178/sst.003.008

The International Pierre Gy Sampling Association (IPGSA) is pleased to announce the launch of its redesigned website, which aims to provide more insight into IPGSA activities and promote educational outreach in the field of sampling theory.



International Pierre Gy Sampling Association

The International Pierre Gy Sampling Association, IPGSA, promotes the development and application of the Theory of Sampling (TOS). TOS was founded by Pierre Gy in the 1950s to address sampling issues in mining and related industries, and since then the IPGSA has applied TOS in manufacturing, pharmaceuticals, agriculture, and waste management.

Learn more about the IPGSA

WCSB12 – Sampling for a Sustainable World

29/06/2026 - 03/07/2026

The IPGSA is pleased to announce that the 12th World Conference on Sampling and Blending (WCSB12) will take place between Monday 29th June and [...]

read more

Euroanalysis 2025 in Barcelona

31/08/2025 - 04/09/2025

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The EUROANALYSIS conference, a biannual international event organized by the Division of Analytical Chemistry of the European Chemical Society, will [...]

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“Introduction to the Theory and Practice of Sampling” available again

We are pleased to announce the re-release of the essential reference work "Introduction to the Theory and Practice of Sampling" by Prof. Kim H. Esbensen. This comprehensive introductory guide to representative sampling is now available through [...]

read more

About IPGSA

The purpose of the International Pierre Gy Sampling Association (IPGSA) is to oversee formal activities of the world sampling community and to represent the views of this community.

The Association is not a legally constituted body, but is a common-interest, unincorporated association of persons solely associated for the common purpose of promoting the interests of the world sampling community and its various activities. The Constitution of the Association incorporates the rules identifying in whom control of the Association and its funds are vested.

Lern more about the association

History

The founder of the Theory of Sampling (TOS), Pierre Gy (1924–2015) single-

Council

The Association is headed by a Council. The Council of the Association has the

Figure 1: Home page of the new website

This updated digital platform will serve as a comprehensive resource hub for students, researchers and professionals alike.

Key Features of the Homepage

News and Events: Regular updates on sampling-related conferences and publications.

Educational Outreach: A key focus of the webpage, with the following resources:

- **Curated Reading List**: Foundational and advanced literature recommendations on the Theory of Sampling.
- **Sampling Resource Library**: Downloadable documents offering practical and theoretical insights on sampling techniques.
- **User Contributions**: A feature allowing users to suggest additional resources, promoting a collaborative and community-driven approach to educational growth.

Sampling Science & Technology: Direct access to this specialized journal of the IPGSA, which covers recent advances in sampling research and practical applications across diverse industries.

World Conference Sampling and Blending (WCSB): Latest news about the upcoming conferences. Access to proceedings and pictures of former conferences.

This new platform reflects IPGSA’s commitment to making sampling knowledge accessible and engaging for a global audience.

Visit www.intsamp.org to explore these features and join the international conversation on sampling excellence.

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[1] HERZOG Maschinenfabrik GmbH & Co. KG, Osnabrück, Germany.

Revised 3rd ed. of Sampling Standard DS 3077

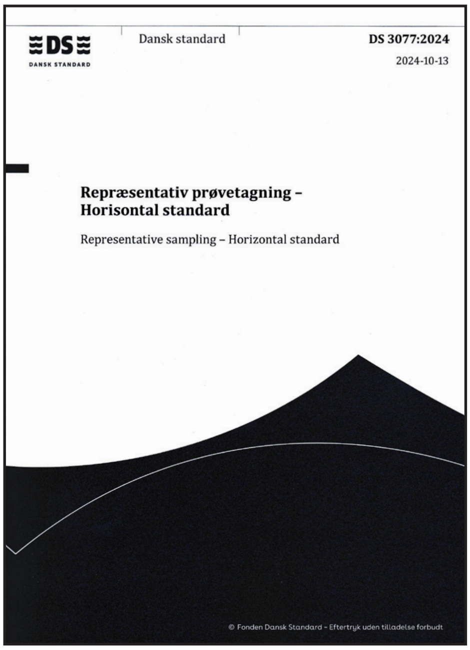
By Kim H. Esbensen[1]

DOI: 10.62178/sst.003.009

The Danish Standard Foundation (DS) announces the publication of DS 3077:2024, the third edition of the generic sampling standard released in October 2024. This edition culminates a 15+ year development project that began in 2008 and succeeds the second edition published in 2013.

Since the millennium‘s start, the Theory of Sampling (TOS) has developed into an axiomatic system with six Governing Principles, eight Sampling Errors, and four Sampling Unit Operations.

This framework led to DS 3077 becoming the world‘s first dedicated standard for representative sampling principles, as documented by Esbensen & Julius (2013). After a decade, this timely third revision updates these foundational concepts.



DS
DANSK STANDARD
Dansk standard
DS 3077:2024
2024-10-13

Repræsentativ prøvetagning –
Horisontal standard

Representative sampling – Horizontal standard

© Fonden Dansk Standard – Eftertryk uden tilladelse forbudt

DS 3077:2024 “Representative sampling – Horizontal standard” aims to serve as the universal standard for sampling all particulate, aggregate and mixture materials, providing authoritative guidance for sampling activities across science, technology, industry, commerce, and regulatory contexts.

The standard can be downloaded at: https://webshop.ds.dk/en/standard/M374267/ds-3077-2024

DS has proposed managing a process to elevate DS 3077:2024 to ISO standard status, with support from the International Pierre Gy Sampling Association (IPGSA).

SCOPE:

“The Theory of Sampling (TOS) is a generic, matrix-independent framework for representative sampling of all types of aggregate and mixture materials (solid, slurries) in all grain-size brackets (from broken ores to powders). TOS’ universal sampling principles can be applied uniformly to all types of materials, and lots composed by aggregate particular matter and slurries. This document describes a generic sampling process in sufficient detail and covers all elements necessary for the stated objective, enabling documentation of sampling representativity under the specified conditions for the sampling process employed. DS 3077 constitutes a complete competence basis for representative sampling, ensuring appropriate levels of accuracy and precision for both primary sampling as well as for all sub-sampling procedures and mass-reduction operations subsequent stages before delivering a guaranteed representative aliquot for analysis. This document outlines a systematic scientific basis for designing new and assessing, and if necessary improving, the performance of existing sampling procedures. The approach described in this document will contribute toward increased reliability in decision-making based on analytical measurement results. This document establishes a basis enabling professional sampling quality control (QC) by mandating disclosure of results from relevant sampling quality objectives (QO): For sampling of stationary lots: Replication Experiment (RE); for sampling of dynamic lots: Variographic Analysis (VA). This document contains an independent macro with variographic software (freeware) making variographic characterisation available for a set of samples restricted to 100 (Annex C).”

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[1] Chairman standard committee S-890 (Danish Standard).

WCSB12 – Sampling for a Sustainable World

By Simon Dominy and Hylke Glass

DOI: 10.62178/sst.003.010

The IPGSA is pleased to announce that the 12th World Conference on Sampling and Blending (WCSB12) will take place between Monday 29th June and Friday 3rd July 2026 in Cornwall UK, hosted by the Camborne School of Mines, University of Exeter.

WCSB12 aims to bring together the diverse international sampling community to present and debate concepts and ideas for a standardised approach to sampling embodied in the Theory of Sampling (TOS).

WCSB12

29th June to 3rd July 2026
Camborne School of Mines, University of Exeter, Cornwall, UK.

The opportunity to meet, exchange ideas, and share practical experiences will be a significant benefit for attendees. The Conference will provide understanding and insights for practitioners, academics, manufacturers and engineering firms aiming to achieve representative sampling through TOS. Topics around societal, industrial, and environmental aspects of particulate sampling in mining/minerals, metals, cement, food and feed, agriculture, aquaculture, and pharmaceuticals will be addressed. Sampling for environmental contamination studies and sustainability are also included.

We look forward to welcoming you to Cornwall in 2026.

Conference Chairs: Professor Hylke Glass and Dr Simon Dominy.

Contributors

Arkenbout, Abel

- Educated in Biology and Toxicology at the University of Utrecht, the Netherlands, (1972-1981).
- Audio engineer, PA, recording, and film music production, K'S d, (1980-1985)
- CEO, Founder Audio & Video Productions Zebra. Development of programmes on transmissible diseases for the Dutch Ministry of Health and initiating Drugs and Information Monitoring System (DIMS) on risks of illicit drugs use(1985-2007).
- CEO and Founder (2011) of a Public Benefit Organisation, ToxicoWatch Foundation
- Research on Persistent Organic Pollutants (POPs) such as dioxins (PCDD/F), dl-PCBs and PFAS related to emissions to the environment from waste incineration. Multi-year biomonitoring studies in Europe on POPs in the environment near (co-) waste incinerations. Participant of technical workgroups commissioned by Governments and industry on data emissions of waste incinerators as independent toxicologist/researcher. (2015-2017)
- CEO and co-founder of ToxicoWatch Consultancy (2017-2025). Head of Research on technical data analyses of POP emissions and residues related to waste incineration, as well a focus on microbiological analytical challenges and potential bioremediation of Substances of Very High Concern.

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- Educated in Marketing Management, followed by work experience in the Advertising & Design, Finance, Notary & Legal service branch as well at the Ministry of Defence, Royal Netherlands Navy/Admiralty, Directorate Naval Construction in the Hague (1982-1995).
- Dendrology through autodidactic teaching and research (1998-2025). Presentations & lectures (2004-2020) as Chair (2006-2012) of Dendrology courses, Leiden.
- Educated Nature/ field biology Guide of the Royal Dutch Natural History Society for field biology (KNNV/IVN) (2007), specialism in dendrology.
- Wool craft designer & Founder of Wool craft business (2010-2020).
- Faculty of Science, Biology at Leiden University, the Netherlands, Assistant associate professor, Biodiversity Animal (invertebrates) (2009-2019).
- Trained professional in the field of toxicology, knowledge through on-the-job research (2015-2025). Staff member & Research team ToxicoWatch Foundation, (2015-2025).
- CEO & co-Founder ToxicoWatch Consultancy (2017-2025).

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Dominy, Simon C.

Dr Simon Dominy is a mining geologist-engineer with over 25 years' experience based in operations, consulting and academia. He has a background in mine operations and technical/leadership roles, with multi-commodity and continent experience. He has worked across the mine value chain from project studies, through to mine reopening/development and operations. Simon is an acknowledged expert in the evaluation and exploitation of coarse gold-bearing high-nugget effect deposits. He has designed and managed numerous studies relating to geometallurgy; resource development; sampling protocol optimisation; bulk sampling programmes; resource/reserve estimation; and grade control. He has authored numerous technical reports (JORC 2012 and NI 43-101), and peer reviewed journal and conference papers. He is a Visiting Associate Professor at the Camborne School of Mines, University of Exeter, UK, and holds technical/advisory positions with Novo Resources Corp., Artemis Resources Ltd., Puma Exploration Inc., and OCX Gold Group. In 2022, Simon was awarded the Pierre Gy Sampling Gold Medal by the IPGSA in 2022.

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Esbensen, Kim H.

Dr Kim H. Esbensen has been research professor in Geoscience Data Analysis and Sampling at GEUS, the National Geological Surveys of Denmark and Greenland (2010–2015), chemometrics and sampling professor at Aalborg University, Denmark (2001–2015), professor (Process Analytical Technologies) at Telemark Institute of Technology, Norway (1990–2000 and 2010–2015). From 2015 he phased out a 35 year academic career for a new quest as consultant and independent researcher. But as he could not terminate his love for teaching, he is regularly active as an international visiting, guest and affiliate professor. A geologist/geochemist/metallurgist/data analyst of training, he has been working 20+ years in the forefront of chemometrics, but since 2000 has devoted most of his R&D to the theme of representative sampling of heterogeneous materials, processes and systems: Theory of Sampling (TOS), PAT (Process Analytical Technology) and chemometrics. He is a member of several scientific societies and has published over 250 peer-reviewed papers and is the author of a widely used textbook in Multivariate Data Analysis, which was published in its 6th edition in 2018. He was chairperson of the taskforce behind the world's first horizontal (matrix-independent) sampling standard DS3077 (2013), 3rd. ed. soon to be inducted as an ISO standard. In 2020 he published the foundational "Introduction to the Theory and Practice of Sampling". Since 2013, he was editor of TOS forum and Spectroscopy Europe/World "Sampling Column", from 2024 amalgamated and metamorphosed into "Sampling Science and Technology" (SST). Kim received the Pierre Gy Gold Medal in 2013 and received the IPGSAs first Distinguished Service Medal in 2024.

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François-Bongarçon, Dominique

Dominique François-Bongarçon graduated as a Mining Engineer and holds a Doctorate in Mining Sciences and Techniques at the Geostatistics Center from the Paris School of Mines (Paris Tech). He has more than 40 years of experience in the mining industry and works as a consultant in earth sciences for his own company, Agoratek International Consultants Inc., based in Canada. In 1992 he embarked on a career-long research in Gy's theory of sampling, and he worked with Pierre Gy as a consultant and on training courses. He contributed to the onset of the WCSB cycle of conferences (2003). In 2009, he was the recipient of the Pierre Gy Sampling Gold Medal. In recent times, he has been continuing his research in Sampling Theory, in the techniques and spirit of the QA-QC discipline and on mine-mill reconciliations. He is also making new advances in the handling of extreme grades in Geostatistics.

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Glass, Hylke

Hylke Glass is Professor at the Camborne School of Mines (CSM), a department of the University of Exeter, since 2001. He was originally introduced to sampling theory by Theo Zegers at the Delft University of Technology in 1994. Togetherthey investigated the quantification of the sampling variance and the effects of grade varying across particle sizes, degree of liberation, the particle size distribution itself, moisture content, and occurrence of very low grades. This led to aa number of publications, including a presentation at the Surface Mining 1996 conference. Following Theo's retirement in 1997, Hylke took over the teaching of sampling of particulate materials and, from 1999, worked with Bas Geelhoed on creating understanding about fundamental aspects of Pierre Gy's Theoty of Sampling (TOS). A series of papers were published in journals including Geostandards Newsletter and Statistica Neerlandica. He continues to take an active interest in the development of sampling theory, its application in resource estimation and control of mineral processing, as well as raising awareness of sampling in the mining, engineering and minerals processing courses taught at CSM.

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Lischka, Martin

Martin Lischka is a geoscientist with a master's degree in geosciences and the environment. He has over nine years of experience in sample preparation and currently serves as the R&D section manager at HERZOG Maschinenfabrik, a company that specializes in automated equipment for sample preparation in the mining industry. Mr. Lischka's work focuses on developing innovative solutions for sample preparation, particularly in the areas of mineral analysis and process automation. He has also been involved in research projects related to precious metal recycling and sensor-based sampling techniques. His contributions are significant in advancing the accuracy and reliability of sample preparation equipment used globally in the mining sector.

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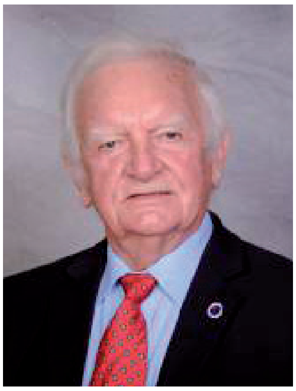

Pitard, Francis F.

Dr Francis F. Pitard is a consulting expert in Sampling, Statistical Process Control (SPC) and Total Quality Management (TQM). He is President of Francis Pitard Sampling Consultants in Broomfield, Colorado, USA. Dr Pitard has six years of experience with the French Atomic Energy Commission and fifteen years with Amax Extractive R&D. He teaches Sampling Theory for the Continuing Education Offices of the Colorado School of Mines. He has a Doctorate in Technologies from Aalborg University in Denmark. He is the author of Theory of Sampling and Sampling Practice (Third Edition 2019). He is the recipient of the prestigious Pierre Gy's Gold Medal for excellence in promoting and teaching the Theory of Sampling.

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Rawle, Alan F.

In May 2024, Alan Rawle put down (or hung up) his spatula, scoop, and spinning riffler (3 Sampling S‘s) for the last time after 34 years tied to the particle characterization industry, a topic he‘d first encountered in his Ph.D. at the very end of the 70‘s (not his 70‘s but the 1970‘s). He has now taken up a full-time career in cat herding and bird watching. In the context of contributing articles to magazines, his nom-de-plume is Phil Space. Alan has a degree in industrial chemistry and a Ph.D. in supported alloy catalysts, both acquired at Brunel University, London, UK. From 1990 to 2024, Alan was with Malvern Instruments (now Malvern Panalytical) and was the Applications Manager based in Westborough, MA, USA since 2003. Dr. Rawle had spent many years working with the ISO TC24/SC4 (Particle Characterization) standardization committee, assisting with the writing of documentary standards in light scattering, small-angle X-ray scattering, image analysis, zeta potential, and dispersion, as well as his own interest in the theory and practice of sampling. He presented Short Courses at Pittcon for over 10 years on these topics. Dr. Rawle was (2005 – 2022) Co-Chair of E 56.02, the Characterization SubCommittee of the ASTM E56 Committee on Nanotechnology. He was the Technical Author (i.e., writer) for ASTM standards in particle sizing, zeta potential, size distribution calculation, among others. Dr. Rawle is also a Fellow of the Royal Society of Chemistry (FRSC), a Distinguished Fellow of the International Engineering and Technology Institute (DFIETI), and a regular contributor to ResearchGate.

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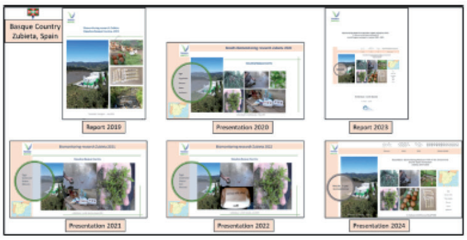

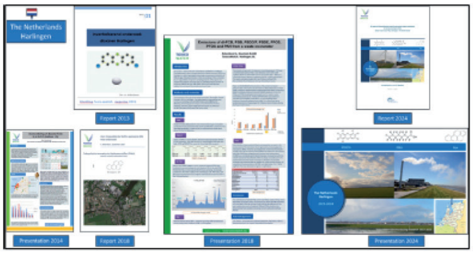

All reports can be downloaded from: **www.toxicowatch.org**

TOXICO
WATCH

Happy Birthday

**Congratulations and best wishes to Kim,
our Editor-in-Chief.**

With your contagious dedication and enthusiasm, you made significant strides in making the Theory of Sampling more accessible and applicable across a wide range of materials and disciplines. Equally important, you have shaped SST into a valuable platform for sharing experiences and fostering scientific dialogue on all aspects of sampling, never forgetting a good touch of sense of humour. Because of your fantastic capacity to enjoy life and your never-ending good spirit, some of us nicknamed you the "King of Sampling"... with the hope that you will continue to guide us with your solid editorial experience!

We wish you continued success, good fortune, and good health in all your future endeavours!

Claudia Paoletti (Vice President IPGSA), Christopher Robben & Benedikt Dolzer

How to contribute

Sampling Science and Technology (SST) serves as a collaborative platform fostering scientific and technological engagement within the global sampling community. Our primary objective is to have a significant educational impact, catering to various levels of interest.

SST embraces didactic studies, practical insights, illustrative case histories, and occasional theoretical articles tailored for the sampling community in both strict and broad senses. Your valuable contributions play a pivotal role in our mission to cultivate professional sampling competence across diverse societal sectors where sampling holds significance — spanning science, technology, industry, trade, food/feed, public health, and more.

Sampling Science and Technology (SST) values scientific literacy and celebrates sincere and honest writing efforts. SST values human learning experiences, human skills, and the unique human abilities to associate, to make inference. SST encourages human educational and didactic enterprises - in deliberate opposition to artificial intelligence (AI) offering lazy technological shortcuts that undermines creative, professional reflection and dismisses the expertise of trained, hard-working scientific and technological authors. SST is very little interested in AI's millifluous language (which indeed is impressive), but there are of course many technical benefits from AI, which should all be fully used, but only with educated, careful supervision and oversight.

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If you have scientific questions regarding a contribution, please contact the Editor-in-chief at khe.consult@gmail.com.

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WCSB12

29 June - 3 July 2026

Camborne School of Mines
University of Exeter
Cornwall, UK

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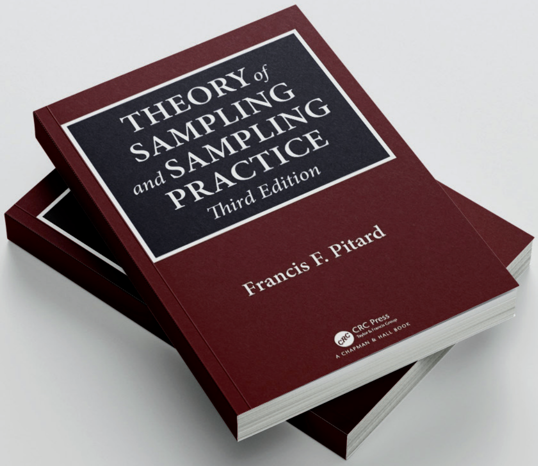
Introduction to the Theory and Practice of Sampling

by K.H. Esbensen

SIX Publishing (2024)

ISBN: 978-3-9826493-1-3
Price: € 85.00

six-publishing.com/tos-introduction



Theory of Sampling and Sampling Practice, 3rd Ed.

by F.F. Pitard

CRC Press, Taylor & Francis Group (2019)

ISBN: 978-1-138-47648-6
DOI: 10.1201/9781351105934
Price: U$ 260.00

amazon.com/dp/113847648X

Theory and Practice of Particulate Sampling: an Engineering Approach

by Geoffrey J. Lyman

Materials Sampling & Consulting (2019)

ISBN: 978-164633382-0
Price: AUD 405.00

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