Metoder til risikohåndtering af nanomaterialer

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Regulatory (REACH) Exposure Assessment

Exposure estimations should describe exposure é relevant for the exposure scenario.

The exposure estimation should, where possible, present both reasonable worst-case and typical exposures. é

To address the reasonable worst-case, it is recommended to select the 90th percentile of the exposure distributioné

Exposure which results from accidents, malfunction or deliberate misuse should not be addressedé

Exposure estimates should be developed by collecting all necessary information (including that obtained from analogous situations or from models)é

REACH modeling tools not validated for NM

- REACH Tier 1 estimates
- ECETOC TRA
- EMKG EXPO Tool
- ConsExpo
- Risk of Derm
- Stoffenmanager
- Advanced REACH Tool
- …

- ñNoò exposure limits or official DNELôs
- No proper emission potentials for NM
- No default exposure scenarios in the tools
- Lack of product categories for nanoproducts
- Gaps in application domains

REACH assessments not possible or should be done with GREAT care!

Standard emission potentials in some REACH R.14 recommended tools and dustiness of MNM

Example: ECETOC-TRA

Table R.14-5: Help on fugacity selection criteria

General description	Relative dustiness potential	Typical materials	TRA Selection Value
Not dusty	1	Plastic granules [a], pelleted fertilisers	**Low**
Slightly dusty	10 - 100 times dustier	Dry garden peat, sugar, salt	**Low /Medium** [c]
Dusty	100 - 1,000 times dustier	Talc, graphite	**Medium**
Very/extremely dusty	More than 1,000 times dustier	Cement dust, milled powders, plaster, flour, lyophilised powders, (process fumes [b])	**High**

[a] Exposures to materials where a substance is contained and bound in a matrix (e.g. pigment within a plastic, filler within paint) should also be included in this category. Although the real exposure is actually determined by a combination of physical form and the bioavailability of the substance within the matrix, because the bioavailability is very low under such circumstances this will result in a low exposure potential.

[b] Process fumes (e.g. rubber, welding, soldering) behave like gases and would be considered within this category if exposures to such complex mixtures are considered in any risk assessment.

[c] The user may choose between low and medium fugacity

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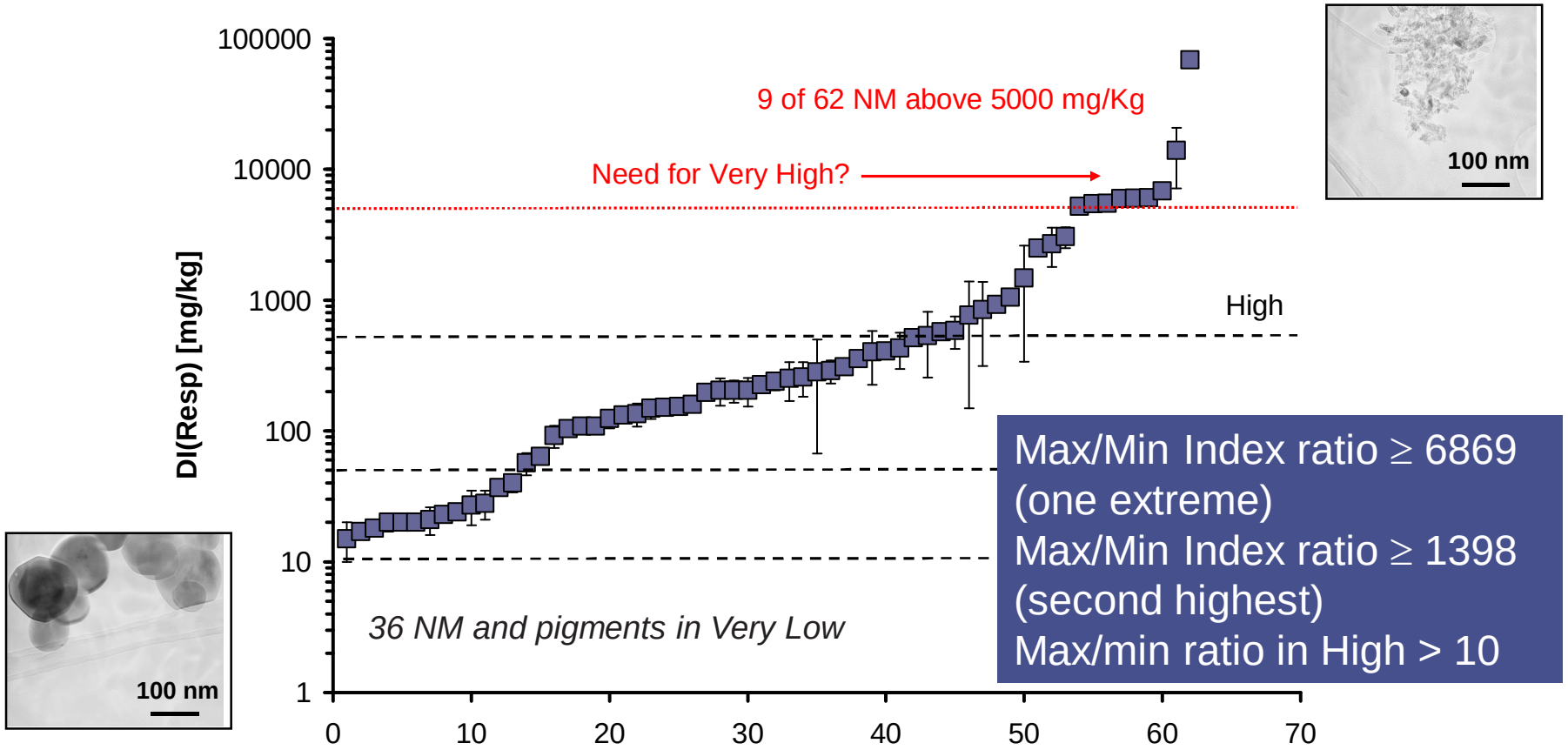
Variation in respirable dustiness index for fine pigments and nanopowders as determined by the EN15051 rotating drum dustiness tester



Max/Min Index ratio ≥ 6869 (one extreme)
Max/Min Index ratio ≥ 1398 (second highest)
Max/min ratio in High > 10

Jensen et al. (unpublished) med data fra a.o.
Schneider and Jensen (2008) Ann. Occ. Hyg.
Jensen et al. (2009) J. Nanopart. Res.
Levin et al. (2014) J. Occ. Env. H.
Levin et al. (2015) J. Nanopart. Res.

Measurements are preferred, but there are Nano Issues for (Occupational) Exposure Assessment

1. Discrimination from background particles
2. High spatial and temporal variability
3. Mass-concentrations may be irrelevant
4. Maximum relevant size(-fractions)?
5. Measurement of size-distribution
6. Measurement of other metrics (n; SA)
7. Measurement of high-aspect ratio NM
8. Suitability of measurement devices

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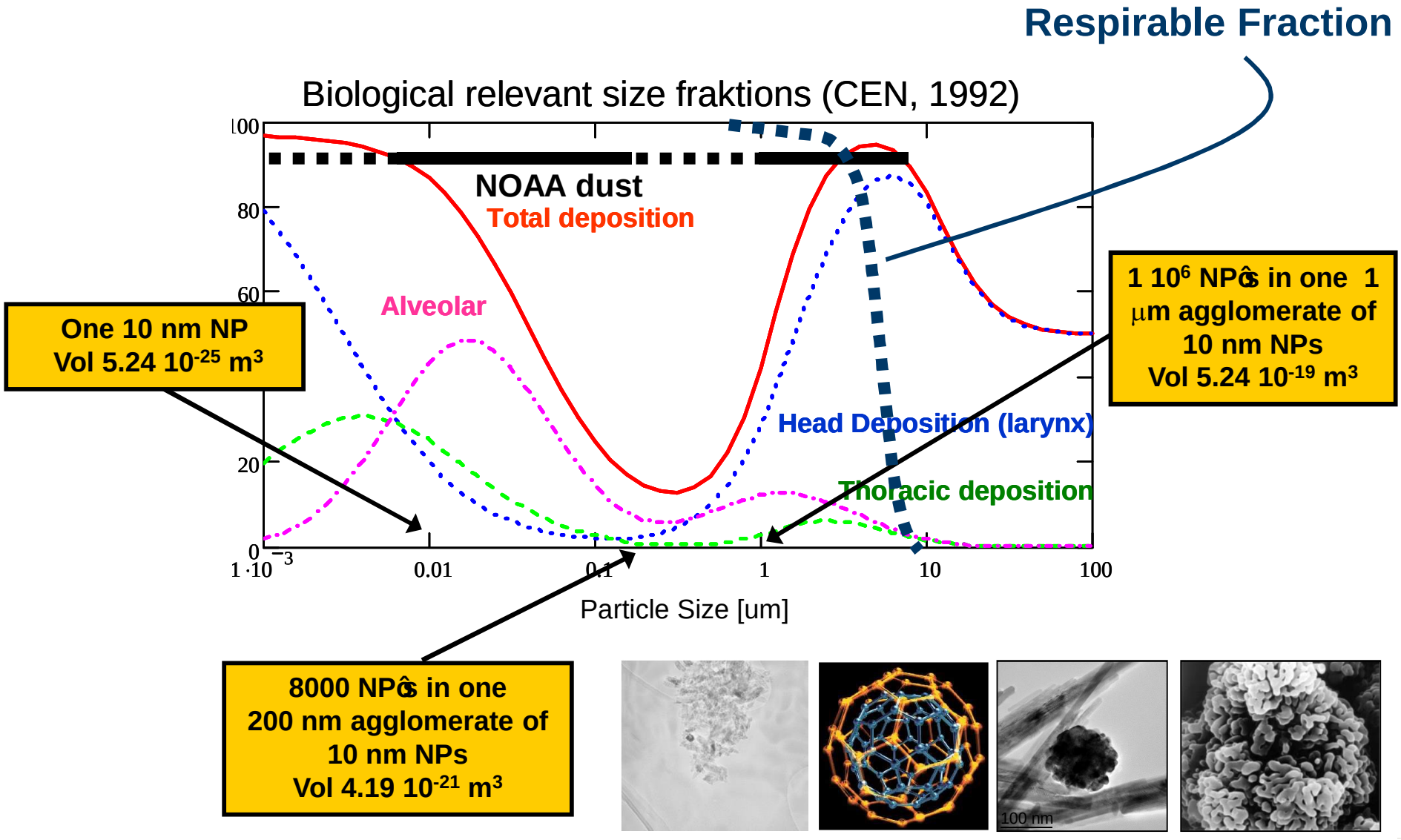
Size-distributions and maximum relevant size?

- Nano-Objects Aggregates and Agglomerates -



What to do until occupational exposure limits are established and REACH methods are modernized?

- **Apply Control banding tools (application of precautionary principles or predicitve models for hazard and exposure assessment)**
  - **Control Banding tools offer a structured procedure by which the hazard and exposure risk of a compound in a given occupational work situation.**
  - **Control Banding metods are often relatively simple, but the most advanced tool are at the same level as the most avanced Tier 1 level in ECHA's REACH guidance R.14.**

- **Stoffenmanager Nano**
- **NanoSafer**

Severity \ Probability	Extremely Unlikely (0-25)	Less Likely (26-50)	Likely (51-75)	Probable (76-100)
Very High (76-100)	RL 3	RL 3	RL 4	RL 4
High (51-75)	RL 2	RL 2	RL 3	RL 4
Medium (26-50)	RL 1	RL 1	RL 2	RL 3
Low (0-25)	RL 1	RL 1	RL 1	RL 2

Control bands:

RL 1: General Ventilation

RL 2: Fume hoods or local exhaust ventilation

RL 3: Containment

RL 4: Seek specialist advice

Paik et al. (2008)

Application domains and Output from the Control-Banding models

Name	NM Definition	Target group/scope	"Outcome" RM recommendation	Ref.
CB Nanotool	ASTM[d]	Nanotechnology Forskere / Risk assessment and management	Risk Level. General recommendations.	Paik et al. (2008); Zalk et al. (2009) .
IVAM Guidance	Own definition similarity with EC	Workers/Occupational Hygiene	Control level bands. General recommendations and reference to hierarchic Occupational Hygiene.	Cornelissen et al., (2011)
Swiss Precautionary Matrix	ISO/TS 27687	Employees, consumers and the environment/ Source identification and risk reduction	Need for action/no action	Höck et al. (2008); Höck et al. (2011); Höck et al. (2013).
Stoffenmanager Nano	ISO/TS 27687 SCENIHR. (2010)	Employers and employees/ Prioritize health risks and implementation of control measures.	Risk priority bands. Ranking priority of needed actions	van Duuren-Stuurman et al. (2012)
ANSES CB Tool	ISO/TS 27687 EC[b]	Small to large enterprises/Exposure prevention	Risk Control Bands. Technical solutions for exposure prevention at work station	Ostiguy et al., 2010; Riediker et al., 2012
NanoSafer 1.0 og 1.1	ISO/TS 27687 EC	SMEs/Precautionary risk assessment	Risk Level. Recommendation and actions to be taken into consideration	Kristensen et al. (2010). Jensen et al. (in prep.) Liguori et al. (in prep.)

From Liguori et al. (under revision)

Key elements and information requirements in the Control Banding models

Estimerer både akut og daglig eksponering ved både process og i lokale

Method Risikokategoriserings-Værktøj (Aktion: Ja/Nej)	Number of Input parameters asked for	Number of input parameters used			Number of control bands		
		Nano-relevance	Hazard scaling	Expo. scaling	Haz.	Exp.	Risk
ANSES CB Tool ¤	9	1	5	3	5	4	5
NanoSafer 1.0 #	25	5	5	13	4	5	5
IVAM Guidance ¤	28	-	2	1	3	3	3
Swiss Precautionary Matrix	28	7	6	6	n.a.	n.a.	2
CB Nanotool	53	-	15	5	4	4	4
Stoffenmanager Nano #	47	-	2	26	5	4	3

¤ The technically simplest model
The technically most advanced models

Estimerer task og kronisk eksponering

Beregnet til vurdering af risici
Ved produktion og anvendelse
af NM i laboratorier

Modified from Liguori et al. (under revision)

Comparative output of the models

❖ **Small-scale activity**

- Process: Gently pouring 5 x 1 g CNT into a beaker; 10 minute breaks; dustiness known to be very low. Annual use: 50 g.
- Work site: Fume-hood in a laboratory (3.5 x 5 x 2.9 m^3); air-exchange rate = 5/h

❖ **Intermediate scale activity**

- Process: Pouring of 5 x 20 kg sacks with surface coated TiO2 into a dry tank; 5 cm gap between sack and lid; dustiness known: 399 mg/kg. Annual use: 12 t/year.
- Work site: LEV in use; (4 x 5 x 4.5 m^3); air-exchange rate = 5/h

❖ **Large scale industrial use activity**

- Process: Pouring 1 x 800 kg big-bag with surface-coated ZnO into mixer from edge at lid; 1 hour, dustiness reported to be moderate. Annuak use: 40 t/year.
- Work site: LEV in use; 8 x 15 x 7 m^3 workroom; air-exchange rate = 10/hour

Materials in comparison

Material		SSA (m^2/g)	D (g/cm^3)	A (nm)	B (nm)	C (nm)	OEL(resp) [mg/m^3]	coated	R-sentence
TiO2	UV-Titan L181	107	4	17	17	17	10.0 TiO_2	Ja	-
ZnO	NM111 (OECD)	15.1	5.66	80	80	80	4.98 ZnO	Ja	-
SWCNT	Short OH-funktionalized	407	2.1	1	2	2000	3.50 carbon black	Ja	R36/R37

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Small scale (short CNT-OH)

- **ANSES:** Full containment and review by a specialist is required
- **IVAM:** According to the hierarchic Occupational Hygienic Strategy, the technical and organizational feasible protective measures are evaluated on their economical feasibility. Control measures will be based on this evaluation. **Fume-hood used in assessment*
- **Stoffenmanager:** High risk. **Fume-hood assumed in assessment; annual use: 50 g.*
- **Nanosafer 1.0:** At highest control level: High toxicity suspected and/or high exposure potential. The work should be performed using highly efficient local exhaust ventilation, fume-hood, glove-box etc. Respiratory protection equipment (P3 or higher quality) may be relevant as supplement and should be be available in case of accidents.

SWCNT	Hazard	Exposure	Control Level
ANSES	5/5	3/5	5/5
IVAM	3/3	2/3	2/3*
Stoffenman. Nano	5/5	Task: 3/4 Time: 2/4	3/3*
NanoSafer	3/4	NF: 1/5 (acute) NF: 1/5 (daily) FF: 1/5 (acute) FF: 1/5 (daily)	3/5

Fume-hood in use and considered the recommendation by NanoSafer due to low exposure levels when working with 1 g SWCNT. The other models recommend higher protection levels.

Intermediate scale (TiO_2)

- **ANSES:** Full containment: continuously closed systems.
- **IVAM:** The hierarchic Occupational Hygienic Strategy will be strictly applied and all protective measures that are both technically and organizationally feasible will be implemented.
- **Stoffenmanager Nano:** Middle (task-weighed) risk score at highest control level. *LEV used in the assessment; annual use: 12,000 Kg*.
- **Nanosafer 1.0:** Very high toxicity suspected and/or moderate to very high exposure. The work should be conducted under strict exposure control, such as in a fume-hood, a separate enclosure etc. Air-supplied respirators or high-efficient filter masks (P3 or higher quality) may used as a supplement and must be readily available in case of accidents. Expert advice is recommended.

TiO_2	Hazard	Exposure	Control Level
ANSES	3/5	4/5	4/5
IVAM	3/3	2/3	3/3*
Stoffenman. Nano	5/5	Task: 3/4 Time: 2/4	2/3*
NanoSafer	2/4	NF: 5/5 (acute) NF: 5/5 (daily) FF: 5/5 (acute) FF: 5/5 (daily)	5/5

LEV in use. The conditions assessed to be associated with middle risk by Stoffenmanager. The other tools recommend strict exposure control such as enclosure due to high exposure risk.

Large scale (ZnO)

- **ANSES:** Enclosed ventilation: ventilated booth, fume hood, closed reactor with regular opening.
- **IVAM:** The hierarchic Occupational Hygienic Strategy will be strictly applied and all protective measures that are both technically and organizationally feasible will be implemented.
- **Stoffenmanager Nano:** Low (time-weighed) to Middle (task-weighed) risk score. *LEV used in the assessment*; annual use: 40,000 Kg
- **NanoSafer: RL5 as previous assessment** requesting strict exposure control**.** At RL2: Low toxicity suspected and/or low to moderate exposure potential. Work should be performed using local exhaust ventilation, fume hoods etc. depending on the work situation. The work may be performed in combination with use of respiratory protection equipment (P3 or higher quality)…..

ZnO	Hazard	Exposure	Control Level
ANSES	3/5	4/5	4/5
IVAM	3/3	2/3	3/3*
Stoffenman. Nano	5/5	Task: 3/4 Time: 2/4	Task: 2/3* Time: 1/4*
NanoSafer	2/4	NF: 5/5 (acute) NF: 4/5 (daily) FF: 3/5 (acute) FF: 1/5 (daily)	NF: 5/5 (acute) NF: 4/5 (daily) FF: 3/5 (acute) FF: 2/5 (daily)

LEV in use. The use of LEV is also recommended by Stoffenmanager NanoSafer and the other tools recommend higher levels of exposure control. In NanoSafer this is due to risk of high exposure at the source

Conclusions

- Existing R.14 REACH models cannot be used for risk assessment of NM
- Alternative methods for risk assessment and management have been developed and can be used until exposure limits and proper exposure data and measurements methods/protocols have been developed.
- Control Banding tools offer such alternative procedures for risk management
- Comparison between Control Banding Tools show that some of them are competetive with Tier 1 R.14 tools in regards to their assessment principles
- Testing of four existing Control Banding tools suggest that they generally give reasonable and consistent information. Stoffenmanager Nano seems to be generally less precautionary than the other ANSES, IVAM and NanoSafer.
- NanoSafer has more dynamic range in the assessment due to application of first order modeling for both acute and daily exposure in both the near-field and the far-field. This appears to give better recommendations for the case-specific needs for exposure control

  (e.g., low exposure potential = lower risk; lower hazard = lower risk).

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