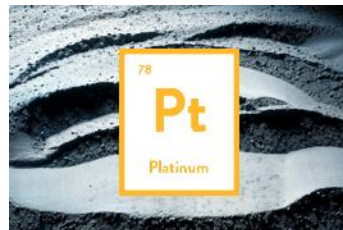
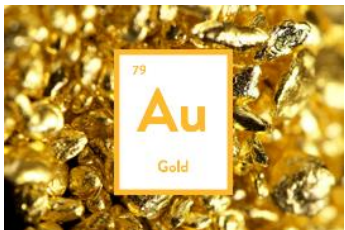
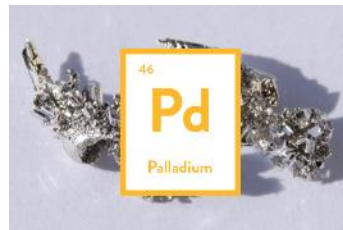
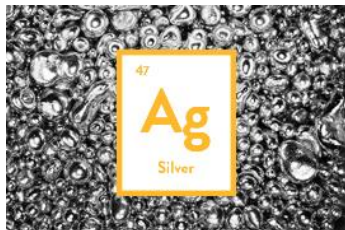




Environmental effects of data-poor metals - *the example of palladium* - *Jelle Mertens, Maxime Eliat-Eliat*

Introduction

- European Precious Metals Federation ('EPMF')
= 8 '*precious*' metals & compounds

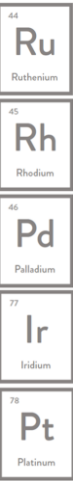


Introduction

- European Precious Metals Federation ('EPMF')
= 8 '*precious*' metals & compounds

'Data-rich'





Introduction

- EU-REACH registrations ‘*data-poor*’ substances
 - n = 67
 - 1-10 tpa: n = 37
 - 10-100 tpa: n = 30
 - **ecotox** data requirements ~ tonnage band

	1-10 tpa	10-100 tpa
Short-term toxicity testing on invertebrates (preferred species <i>Daphnia</i>)	✓	✓
Growth inhibition study aquatic plants (algae preferred)	✓	✓
Short-term toxicity testing on fish		✓
Activated sludge respiration inhibition testing		✓

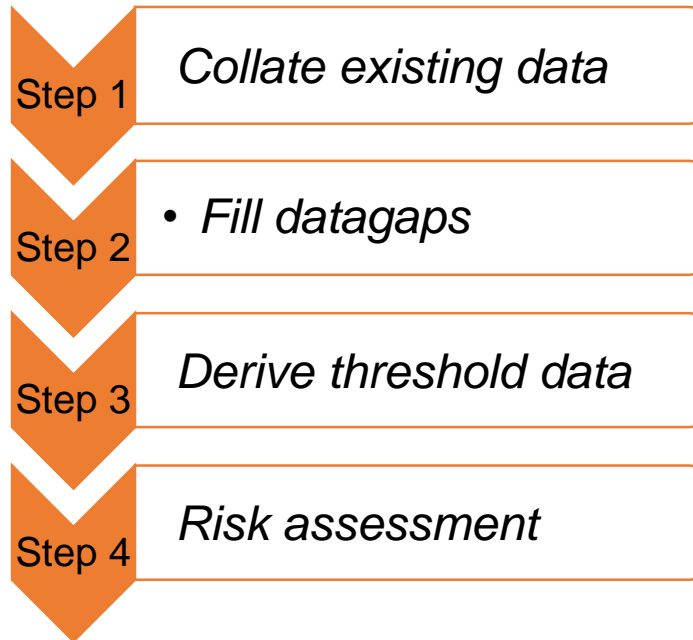
→ **basis for risk assessment**



Introduction



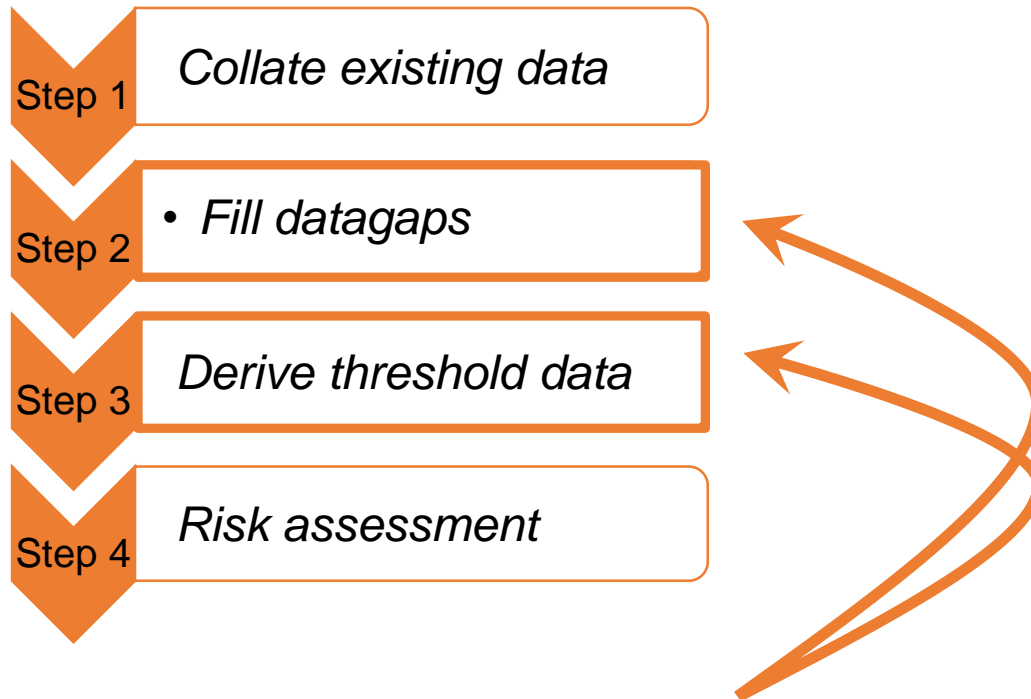
- Generic approach risk assessment:



Introduction



- Generic approach risk assessment:

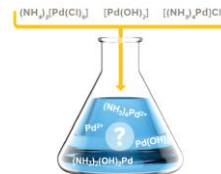


- Key question: **grouping** possible?

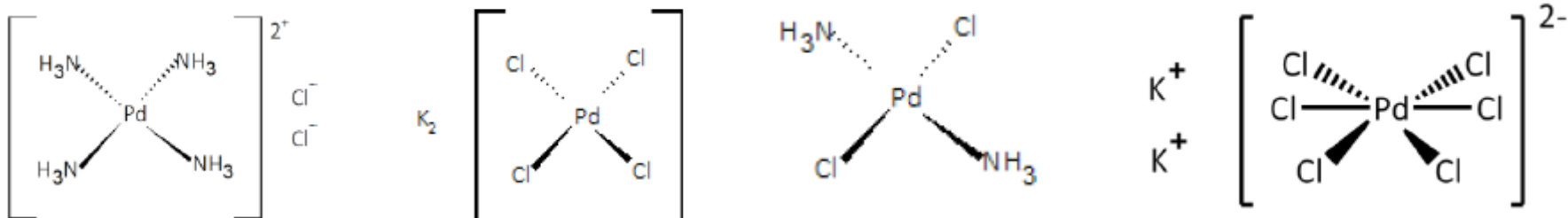
! Various **challenges** for PGMs!

Palladium as example

Pd chemistry

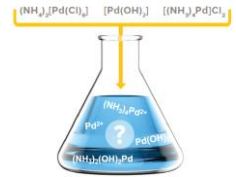


- Palladium-group = palladium metal + 18 palladium compounds
incl. **coordinated complexes**



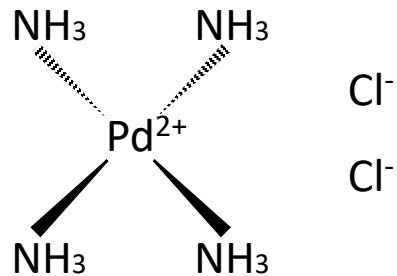
- Palladium = Platinum Group Metal
 - strong **coordinating properties** with (in)organic ligands
 - Pearson (1963): '*PGM = soft acid, prefer to coordinate to soft ligand*'
- $\text{Cl}^- < \text{NO}_3^- < \text{OH}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{NO}_2^- < \text{PPh}_3 < \text{CN}^- < \text{CO}$

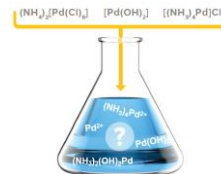
Pd chemistry



- Behaviour Pd salt in aquatic medium
 - scientific consensus:
 - **dominance Pd(II)** species (rapid reduction $\text{Pd}(\text{IV}) \rightarrow \text{Pd}(\text{II})$)
 - **free $[\text{Pd}^{2+}]$ low**
 - speciation:

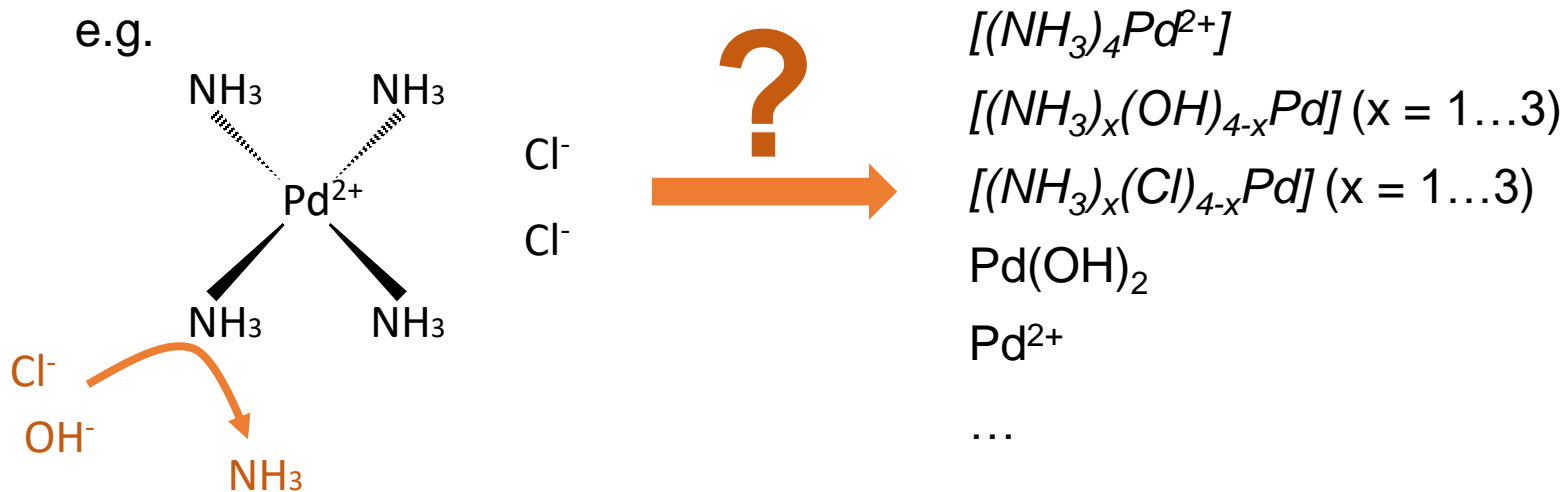
e.g.





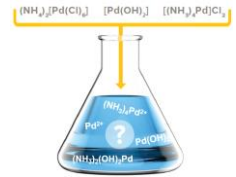
Pd chemistry

- Behaviour Pd salt in aquatic medium
 - scientific consensus:
 - dominance Pd(II)** species (rapid reduction Pd(IV) → Pd(II))
 - free [Pd²⁺] low**
 - speciation:



Unknown combination of Pd ionic species

Pd chemistry



- **Re-speciation** depending on
 - Pd test compound
 - physico-chemical conditions in medium (*pH, Cl, ammonia...*)
- Speciation **modelling** capacity limited: many thermodynamic constants with main ligands lacking

- **Working hypothesis:**

NH_3 -coordinated Pd(II) complexes $\rightarrow [(NH_3)_x(OH)_{4-x}Pd]$ - type complexes

Cl-coordinated Pd(II/IV) complexes
other Pd salts $\left. \vphantom{\begin{matrix} Cl-coordinated Pd(II/IV) \\ other Pd salts \end{matrix}} \right\} \rightarrow [Pd(OH)_x]$ - type complexes



Pd ecotoxicity

- **Published** literature data limited
 - Pd chloride as test compound
 - limited endpoint coverage (*mainly aquatic*)

	Literature data			
	<i>Micro-organisms</i>	<i>Algae</i>	<i>Invertebrate</i>	<i>Fish</i>
Aquatic	2	2 / 0	3 / 0	1 / 0
Sediment	0	NR	1	NR
Soil	0	NR	2	NR



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Pd ecotoxicity

- **Published** literature data limited
 - Pd chloride as test compound
 - limited endpoint coverage (*mainly aquatic*)
 - focus on **acute** endpoints

DATA GAP FILLING

- incl. IND test compounds
- incl. **chronic** endpoints

	Literature data				Industry data			
	<i>Micro-organisms</i>	<i>Algae</i>	<i>Invertebrate</i>	<i>Fish</i>	<i>Micro-organisms</i>	<i>Algae</i>	<i>Invertebrates</i>	<i>Fish</i>
Aquatic	2	2 / 0	3 / 0	1 / 0	4	5 / 5	5 / 3	3 / 0
Sediment	0	NR	1	NR	0	NR	1	NR
Soil	0	NR	2	NR	0	NR	0	NR



Pd ecotoxicity

- Overview aquatic **thresholds**
 - acute effect as *LC50, EC50*
 - chronic effect as *LC10, EC10 or NOEC*
 - only measured dissolved Pd (in $\mu\text{g Pd/L}$)

	fish		invertebrates		algae		micro-organisms
	<i>acute</i>	<i>chronic</i>	<i>acute</i>	<i>chronic</i>	<i>acute</i>	<i>chronic</i>	<i>acute</i>
palladium dichloride	/	/	13	/	6;7		230;610
tetraamminepalladium cmpds (n=2)	190	/	47	36	3	2	13;19
diamminedichloropalladium	154	/	35	>14	2	1	31
tetrachloropalladate cmpds (n=2)	>20	/	29	/	4	1	/
palladium di(4-oxopent-2-en-2-oate)	/	/	76	2	11	5	41
palladium nitrate	4.6×10^4	/	680	/	25	16	/

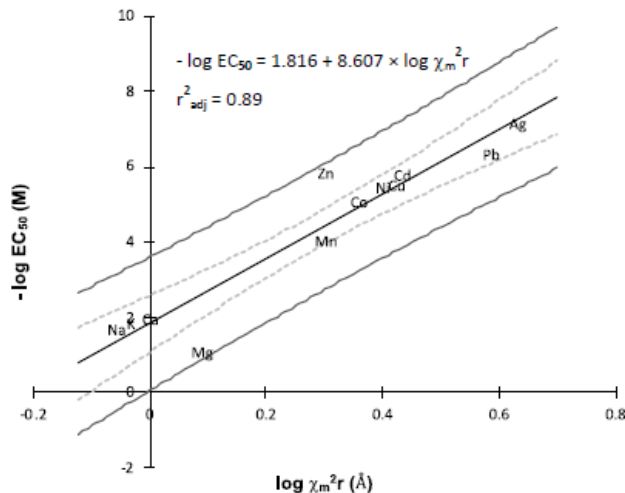
fish least sensitive ↔ algae most sensitive

chronic thresholds 1-3x lower than acute



Pd ecotoxicity

- Pd **sensitivity**: fish < invertebrates < algae
 → confirmed by **QICAR** (*Quantitative Ion Character Activity Relationships*):
 predict acute EC50 value for fish, invertebrates and algae for metals
 using covalent index ($\chi_m r^2$)



Predicted EC50 values ($\mu\text{g Pd/L}$) [95% CI]

fish 29 [5 – 170]

invertebrates 12 [1.5 – 90]

algae 8 [1 – 50]

→ **OK for experimental Pd data**

cfr. presentation Séverine Le Faucheur et al. (Tue 28 May (9.35) Room 101)



Pd ecotoxicity

- **Focus on algae** as most sensitive species

→ How to derive thresholds?

1 value for all Pd compounds
or
distinct value per group?

	algae	
	<i>acute</i>	<i>chronic</i>
palladium dichloride	6;7	
tetraamminepalladium cmpds (n=2)	3	2
diamminedichloropalladium	2	1
tetrachloropalladate cmpds (n=2)	4	1
palladium di(4-oxopent-2-en-2-oate)	11	5
palladium nitrate	25	16

← **organometallic**-type substance

← **UVCB** substance, appearing as mixed NO₃-(hydr)oxo complexes





Pd ecotoxicity

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Specific chemistry, separate assessments





Pd ecotoxicity

- **Focus on algae** as most sensitive species

→ How to derive thresholds?

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	algae	
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thresholds **similar** between
cmpds
→ **grouping !?**

Suggested lowest threshold value Pd: 1...2 µg Pd/L

Conclusions



- Palladium has strong **coordinating** properties
- Coordination complex **depends on physico-chemistry**
- **Uncertainties** on **speciation** in test media & natural environments
- **Little ecotoxicity data** available
- **Algae** suggested as **most sensitive** species
- Existing ecotoxicity data suggest **comparable ecotoxicity threshold** values for Pd salts (incl. coordination complexes)



THANK YOU

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