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RESEARCH INSTITUUT VOOR DE GROENE RUIMTE

From Science to standardization, a necessary step to include bioavailability in risk assessment

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Alterra, Wageningen-UR

Bewertung von Schadstoffen om Flächenrecycling und nachhaltigen Flächenmanagement auf der basis de Verfüchbarkeit/Bioverfüchbarkeit (BioRefine)

07. und 08. Oktober 2009 in Berlin

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Soil and site assessment

- Chemical measurement (tota… …ntrations)
- Ecological and bi… …assays
- Field… …ements
  - (con… …ination/soil compaction)

BIOAVAILABILITY

What do scientists know?

- Total concentrations over estimate risks
- Risk assessment should be based on available concentrations
- We do understand bioavailability
- We have several methods to measure bioavailability

- We still discuss about definitions
- Your method is the best one and should be used all over the world

What do regulators/administrations know?

- Long experience with total concentration
- Total concentrations can be measured reliable
- Many standard procedures available
- Many ‘scientific’ assessment procedures

- Risks are overestimated
- Limited finances available to remediate all contaminated sites
- Public acceptance of measures is important

What do regulators/administrations want?

- A risk assessment they can explain
  - Why is this heavily contaminated site not risk full
- Use of methods that are also used by others
- Clear results and no further discussion
- Cheap and simple

STANDARDIZATION

Standard method

Science

- Many methods available

Scientific goal
- Complex world to be solved with different methods
- Early standardisation leads to misunderstanding of the processes
- Complex methods

interaction

Assessment goal
- Equal treatment
- Comparability
- Without standardisation no system for decision making
- Simple methods

Regulation, administration:

- Give me 'the' method to measure bioavailability of contaminants

From science to regulation: Standardization
ISO/TC190 Soil Quality Working group 'Bioavailability'

What kind of standards

- Connecting chemistry and biology
- Limited set of methods
- Taking into account present regulations
- Scientific base

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First step

ISO 17402 Soil quality — Guidance for the selection and application of methods for the assessment of bioavailability of contaminants in soil and soil materials, 2008

- Conceptual framework
- Direction for use and further development of methods

Definition

ISO 17402

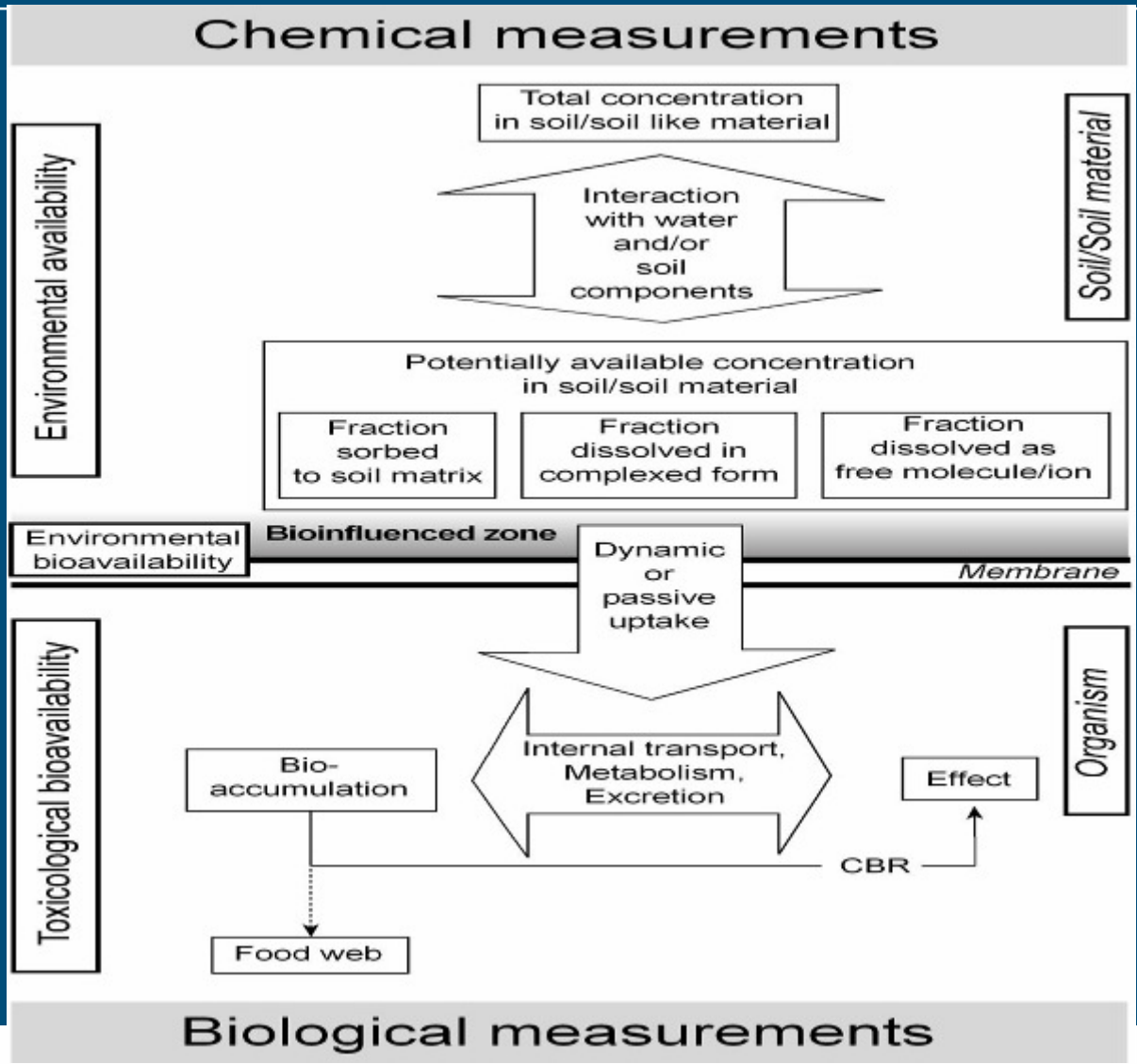
Bioavailability is the degree to which chemicals present in the soil matrix may be absorbed or metabolised by human or ecological receptors or are available for interaction with biological systems (ISO 11074)

- time?
- Different availabilities for different receptors?

- Conceptual
  - The amount that can be transported to the bio-influenced zone and affect organisms within a defined time
- Operational
  - define organism and effect
  - define conditions
  - define time
- Tool
  - How to predict?

Concept of bioavailability

ISO 17402



Operational definition

ISO 17402, Harmsen, 2007

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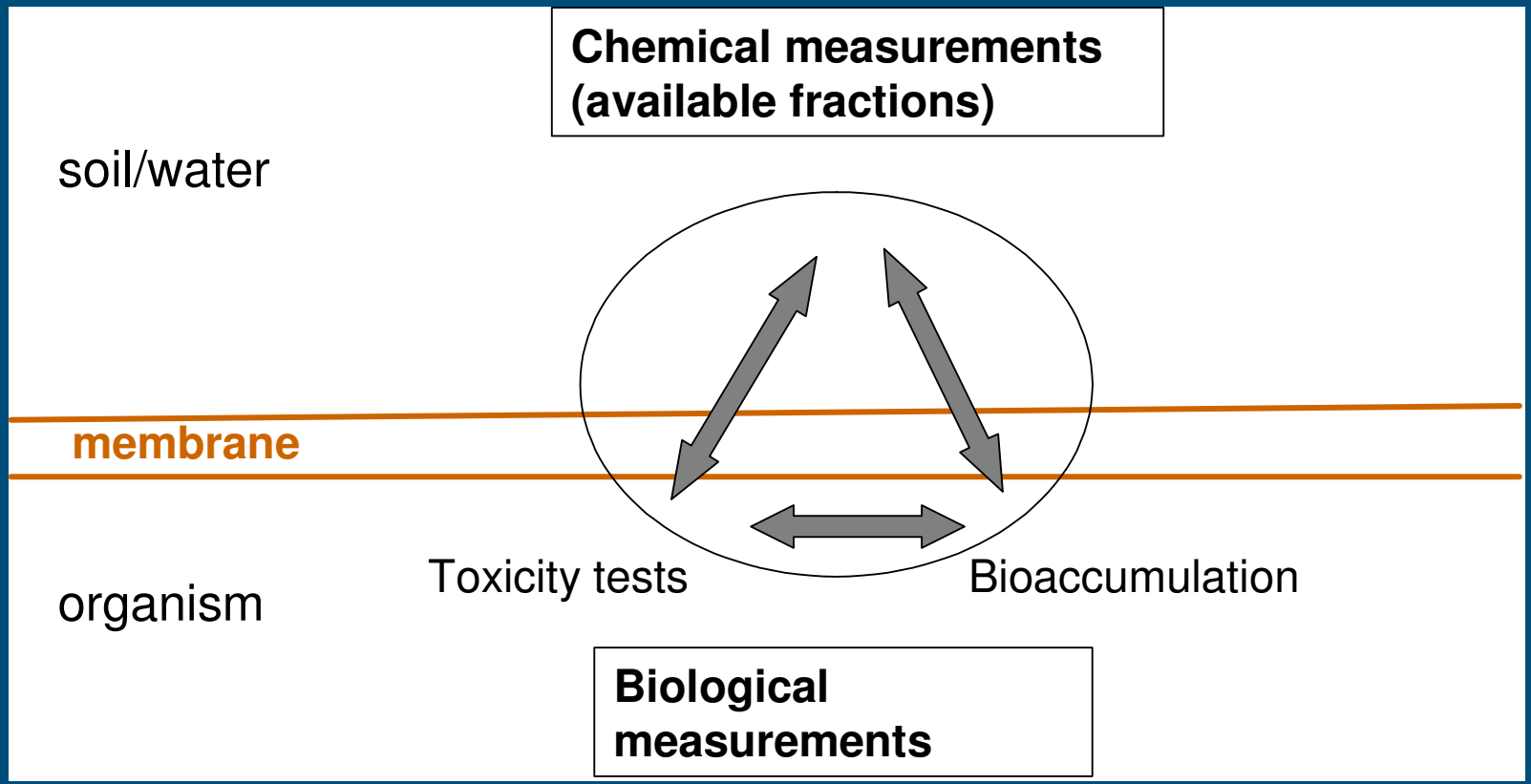
Concept Bioavailability

ISO 17402



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Bioavailability in relation to assessment of soil function

ISO 17402

- Soil functions and organisms to protect
- Risk assessment
- Protection goals

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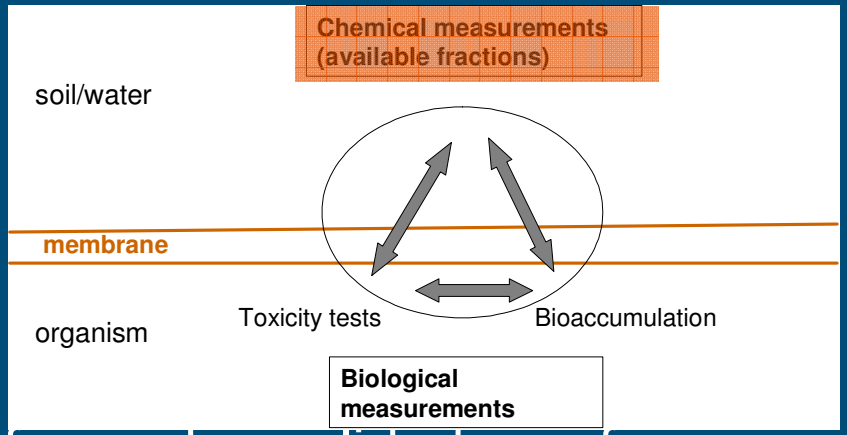
Chemical methods to assess bioavailability

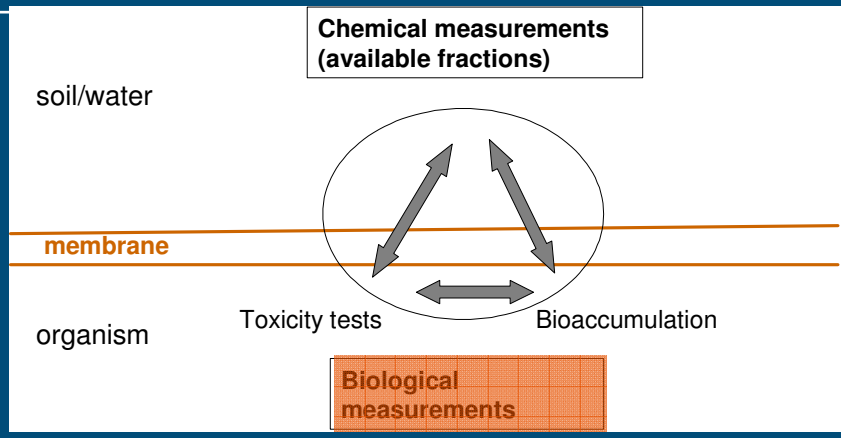
ISO 17402



- water- based extractions;
- concentration in pore water;
- extraction from the water (use of an extra solid phase for exhaustive extraction of the water phase);
- adsorption tools that mimic behaviour of organisms;
- solvent-based extractions;
- weak solvent;
- short extraction or extraction with smaller energy input;
- weak acid or complexing agent (heavy metals) extractions.

Biological/ecotoxicological methods to assess bioavailability

ISO 17402



- molecular level;
- cellular level;
- metabolic level (enzymatic activities or biomarkers);
- individual level (accumulation, mortality, growth, reproduction, behavioural responses);
- population level (abundance, diversity);
- community level (species composition).

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Pathways and chemical methods

ISO 17402

- Human
  - Soil ingestion — Methods for soil ingestion
  - Dermal contact — Methods for dermal uptake
  - Inhalation of soil
  - Groundwater used for drinking water — Methods for leaching
- Exposure of higher animals
- Exposure of soil micro-organisms — Methods for biodegradation
- Exposure of soil invertebrates (micro-, meso- and macro-fauna) — Methods for soil organisms
- Exposure of plants — Methods for plants

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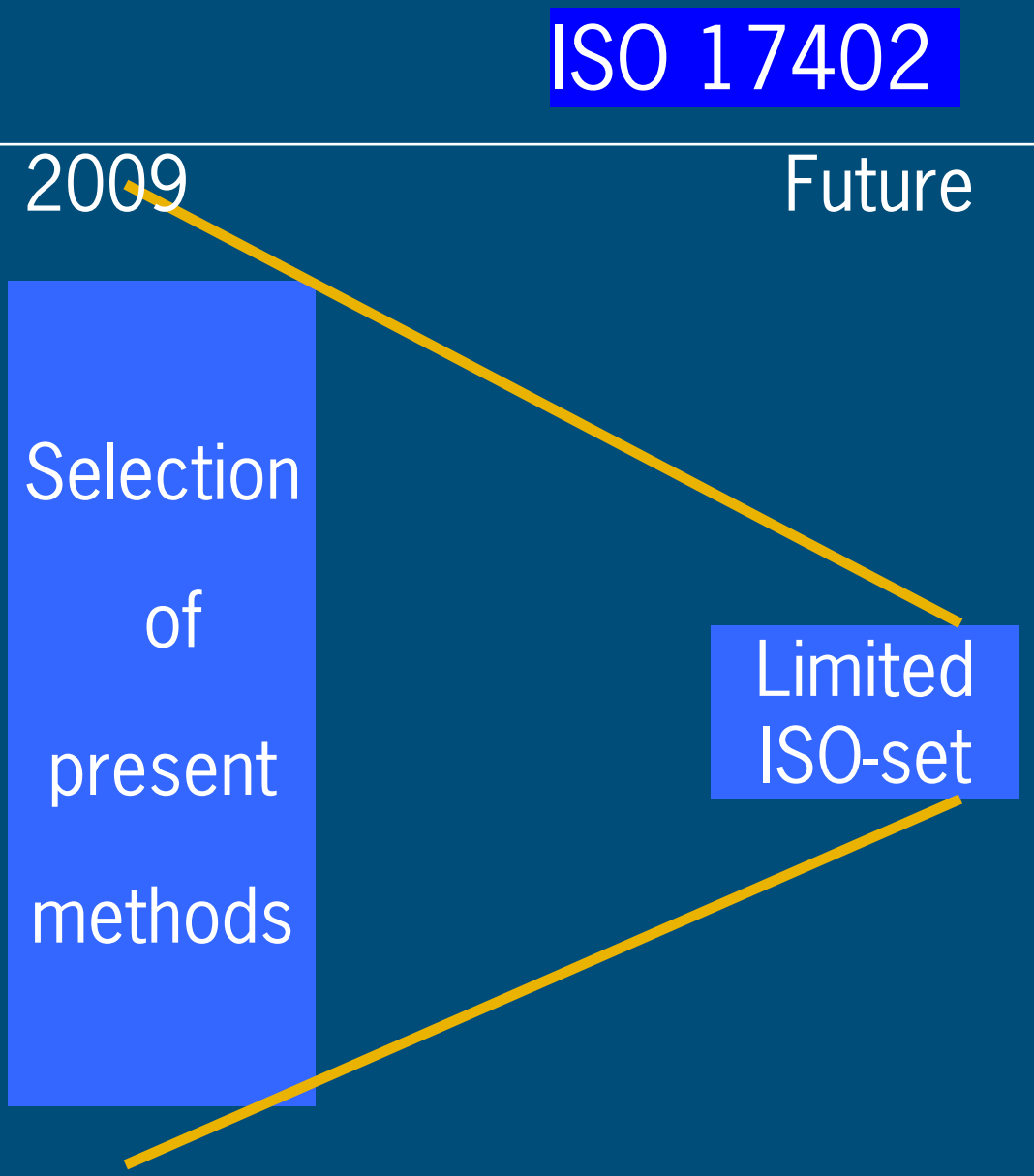
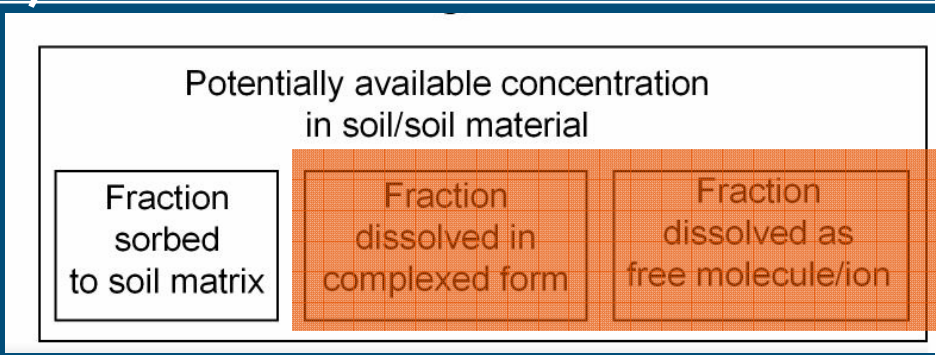
Requirements

- Selection
- Application
- Development



Heavy metals (pore water)

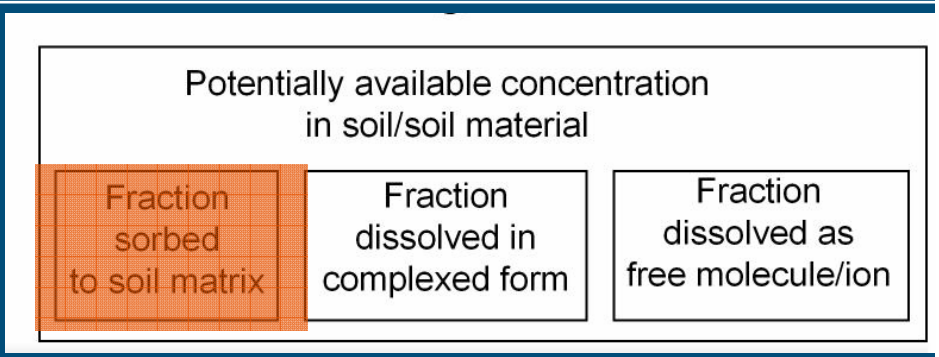


neutral extract

- Present standards
- Present regulations
- Present practice

- ~~0.01 M $CaCl_2$ nutrients (ISO 14255)~~ Decreases DOC
- 0.001 M $CaCl_2$ leaching (ISO 21268-2)
- 1M NH_4NO_3 plant uptake, German regulation (ISO 19730)
- ~~1 M KCL nutrients ISO (ISO 14256)~~ Limited Scope

Heavy metals (sorbed)



Acid extract

- Present standards
- Present regulations
- Present practice

- ~~Aqua regia , ISO 11466)~~ To strong
- 0.43 M HNO_3 (Netherlands)
- 1 M HCl (Japan)

Acid extract → pore water = transfer function

$C_{pore\ water} = f(C_{acid\ extract}, pH, clay, OM, DOC)$

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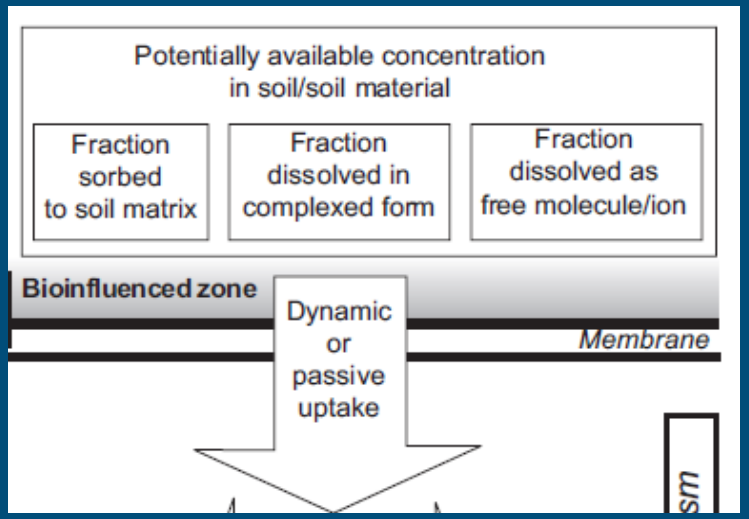
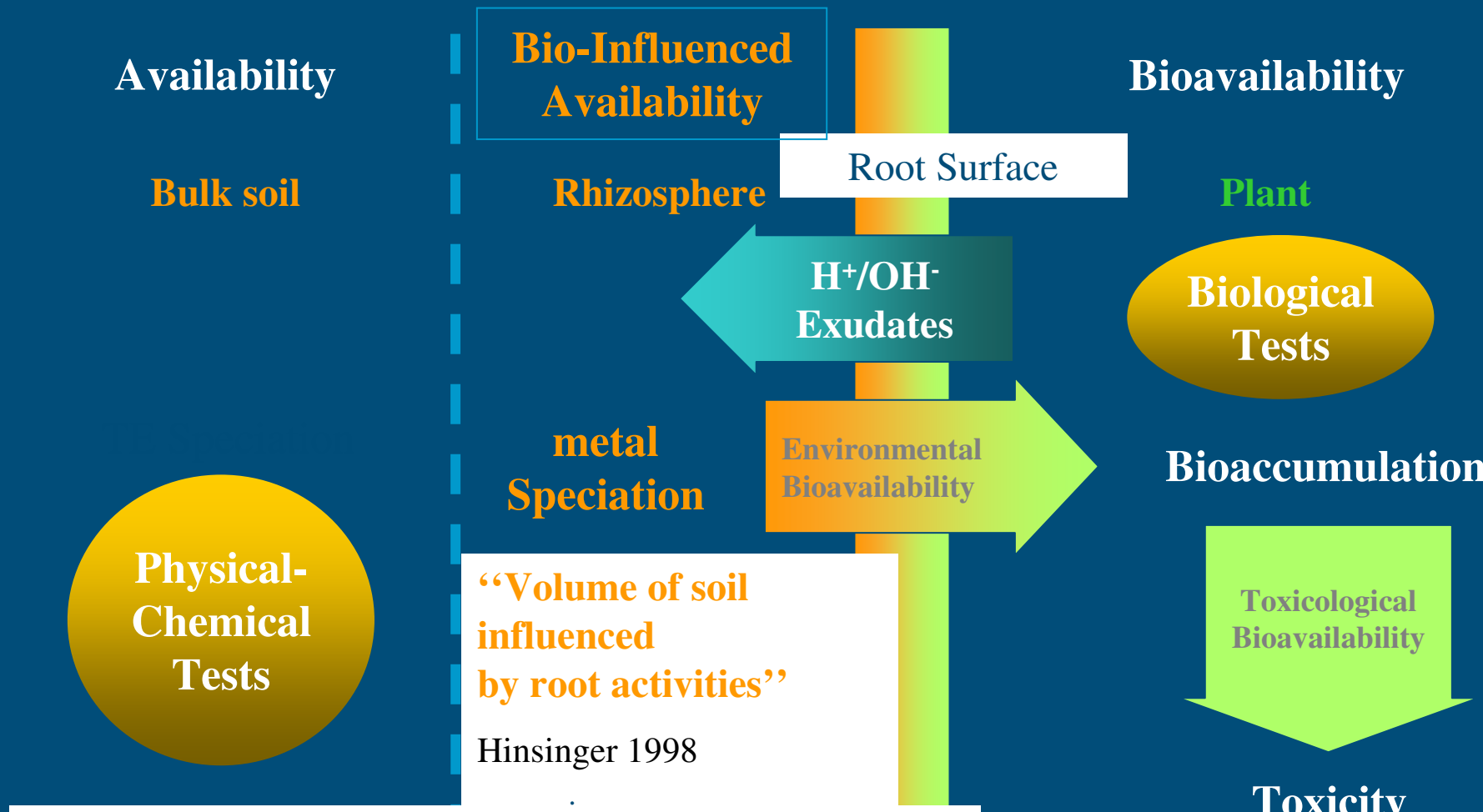
Heavy metals (into the organism)

- Non equilibrium, dynamic approach
  - DGT
  - Kinetic extracts
- Toxicological availability
  - Different ISO standards
- Bioaccumulation



Plants do not react standard (Matthieu Bravin)



Lanno et al. 2004, Ecotox. Environ. Safe.; ISO 17402, 2008

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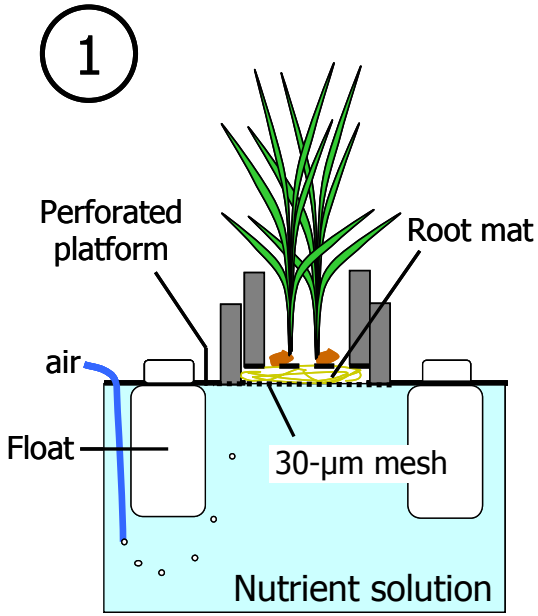
Development of standard biological test

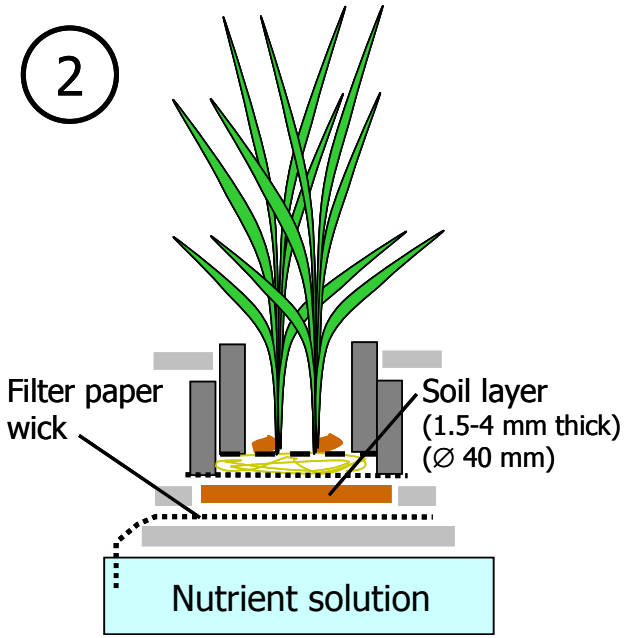
- Use present knowledge
- Should fit in the ISO-framework
- Simple and cheap
- Applicable all over the world
- Scientific basis
- Make planning in agreement with ISO-working group
  - Description of method
  - International acceptation
  - Validation
  - Supply drafts and data

RHIZOtest: a Plant-Based Biotest to Assess the Environmental Bioavailability of Trace Elements to Plants in Contaminated Soils

M. N. Bravin , A. Bispo and P. Hinsinger, France



Preculture period
in hydroponics
2 to 3 weeks



Test culture period
Soil-plant contact
1 week

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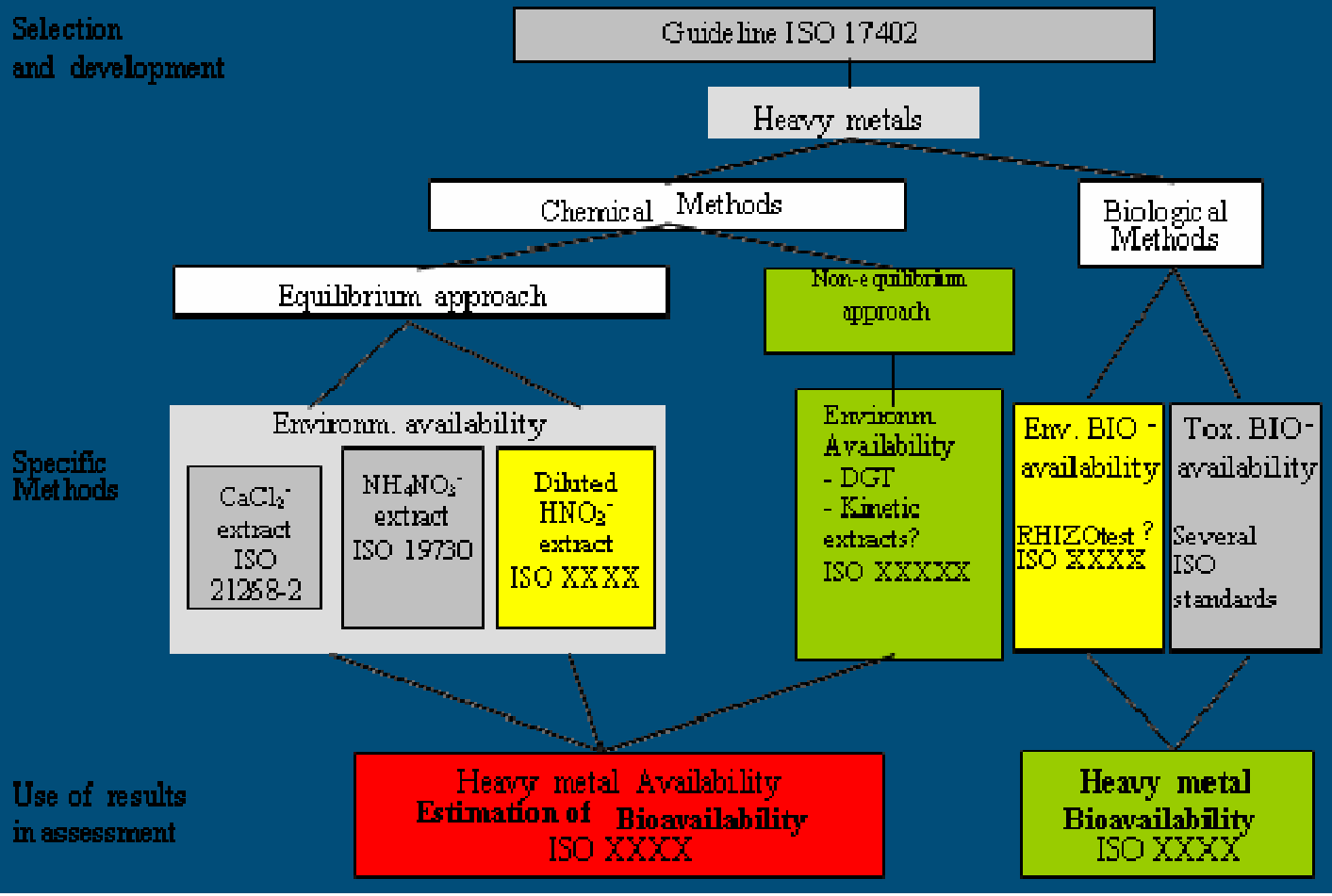
Bioavailability and risk assessment

- What to do with all the results
  - Soil extracts
  - Biological tests
  - Toxicological tests
- Soil quality — Assessment of the environmental bioavailability in soil — Use of soil extracts for the measurement of metal availability and the estimation of metal bioavailability to organisms
- Understand what you have measured
  - Applicability
  - Calibration
  - Modeling

Soil quality — Assessment of the environmental bioavailability in soil — Use of soil extracts for the measurement of metal availability and the estimation of metal bioavailability to organisms



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Multi-surface geochemical modeling of leaching processes (Rob Comans)

"Available" concentrations:
→ Leaching/extraction at low pH (≈0.5)

Major ion chemistry:
pH, major (competing) ions, inorganic ligands
(NIST-thermodynamic database)[1]

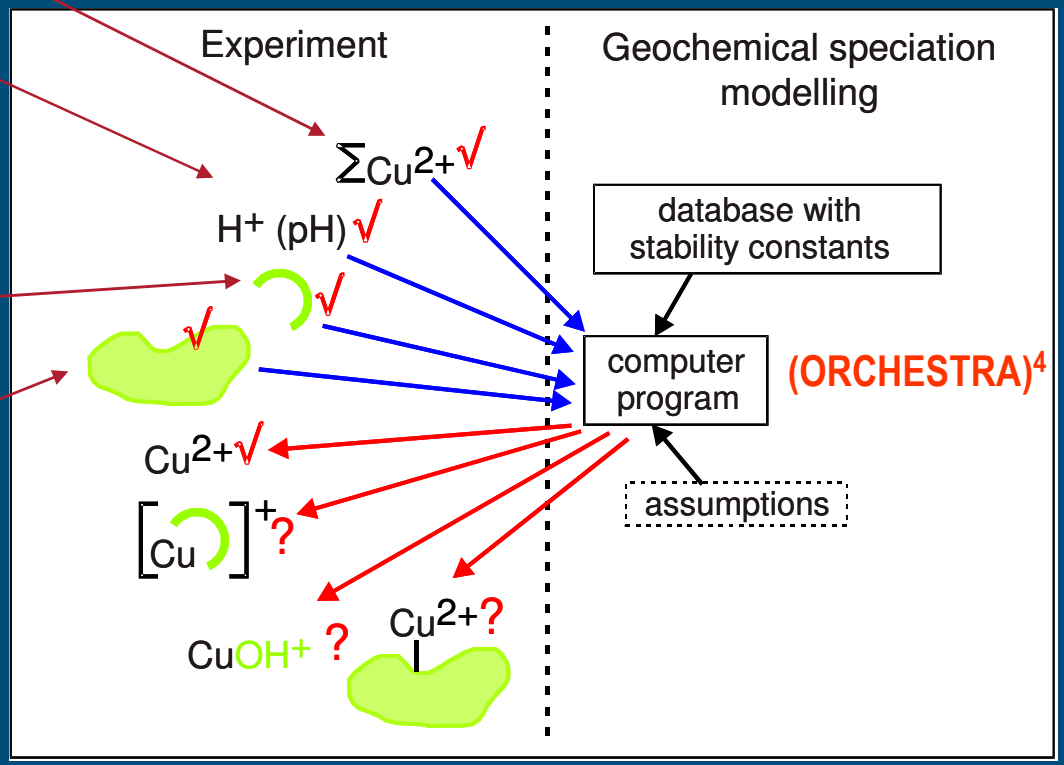
Dissolved organic matter:
Humic and fulvic acids
(NICA model)[2]

Reactive surfaces in the solid phase:
- OM (humic/fulvic acids)

(NICA model)[2]
- Fe/Al (hydr)oxides

(Two layer SCM)[3]
- Clay particles

(Donnan model)



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[1] MINTEQ 4.0/NIST; [2] Milne et al. (2003); [3] Dzombak & Morel (1990); [4] Meeussen (2003)

Consequences modeling

- Soil:
  - pH
  - clay
  - organic matter
  - Fe/Al-oxides
- Extract:
  - ionic strength
  - composition of macro parameters
  - pH
  - dissolved organic matter
  - all other compounds that may form complexes with metals and are known to be present in the soil sample

Calibration

Method	Compo-nents*	Biological target	Endpoint considered for the calibration	Remarks	Reference
$CaCl_2$	Cu	yeast		Include pH	Van der Zee et al., 2003
$CaCl_2$	Cu, Cd, Zn, Pb, Ni	Plant, *Lolium Perenne*	Environmental Bioavailability Root uptake	Include pH	Kalis et al., 2006
$CaCl_2$	Ni	*Avena sativa*	Toxicological Bioavailability Shoot production		Semenzin et al., 2007
$CaCl_2$	Cd	12 genotypes in paddy rice fields	Toxicological Bioavailability Root and Grain Bioaccumulation	Soil samples taken in dewatered fields before the harvest	Römkens et al., 2008
$CaCl_2$	Zn	Springtail *(Folsomida Candida*			Smit et al., 1997
$CaCl_2$	Cd, Pb	Snail *(Helix aspersa)*	Toxicological Bioavailability Concentration in the hepatopancreas	Include pH and OM. 0 to 28 d exposure to spiked soils	Gimbert et al., 2006

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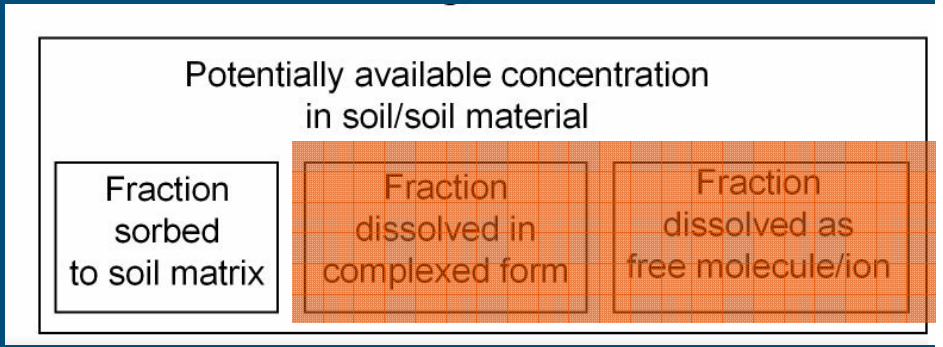
Organic contaminants

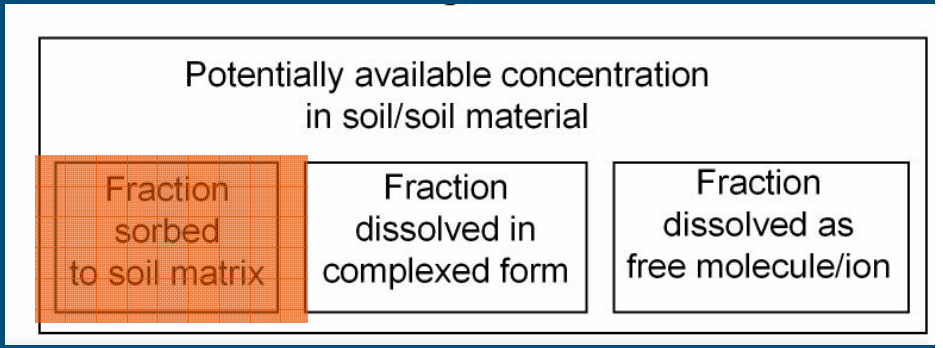
- K_{OC} < 3 (volatiles, modern pesticides)
- K_{OC} > 3 (PAH, PCB, dioxins, PBFR)

Organic contaminants

- Soluble in water
  - ~~Direct measurement~~
  - Passive sampler



- In equilibrium with water
  - Strong adsorbent
  - Tenax, cyclodextrine



Standard structure organics

Planning

ISO 17402 Soil quality — Guidance for the selection and application of methods for the assessment of bioavailability of contaminants in soil and soil materials

Passive sampling 3

Strong adsorbent 1

TENAX, cyclodextrine

Soil quality — Assessment of the environmental bioavailability in soil — Use of adsorbents for the measurement of organics availability and the estimation of organics bioavailability to organisms 2

Related ISO activities

- ISO ISO/TS21269 1-4
- Leaching procedures for subsequent chemical and ecotoxicological testing of soil and soil materials - Part 1: Batch test using a liquid to solid ratio of 2 l/kg dry matter.
- Leaching procedures for subsequent chemical and ecotoxicological testing of soil and soil materials - Part 2: Batch test using a liquid to solid ratio of 10 l/kg dry matter.
- Leaching procedures for subsequent chemical and ecotoxicological testing of soil and soil materials - Part 3: Up-flow percolation test.
- Leaching procedures for subsequent chemical and ecotoxological testing of soil and soil materials - Part 4: Influence of pH on leaching with initial acid/base addition.

Related ISO activities

ISO 17294

- Soil quality - Assessment of human exposure form ingestion of soil and soil material - Guidance on the application and selection of physiologically based extraction methods for the estimation of the human bioaccessibility/bioavailability of metals in soil

ISO/CD 11504

- Soil quality – Assessment of impact from soil contaminated with mineral oil + methods based on existing standards for mineral oil (C_{10}-C_{40}) and volatiles

Concluding remarks

- Scientists and regulators want comparable things
- Standardization is more than description of a method
- Standardization should give:
  - Guidance in choice, application and development, ISO-17402
  - Support in using results of measurements (new activity)
  - Description of limited set of methods (new activity)
- International cooperation and consensus is necessary
- State of the art
- Suitable for heavy metals and organics

With thanks to

ISO/TC190 Working group bioavailability

Berlin, 2009

Australia, 2007

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SETAC Europe

Seville 2010

Society of Environmental Toxicology and Chemistry

SETAC Europe 20th Annual Meeting

"Science and Technology for Environmental Protection"

23 - 27 May 2010 - Seville, Spain

SETAC Europe

Seville 2010

SETAC Europe 20th Annual Meeting, Seville
Science and Technology for Environmental Protection