HRABÁK, PAVEL

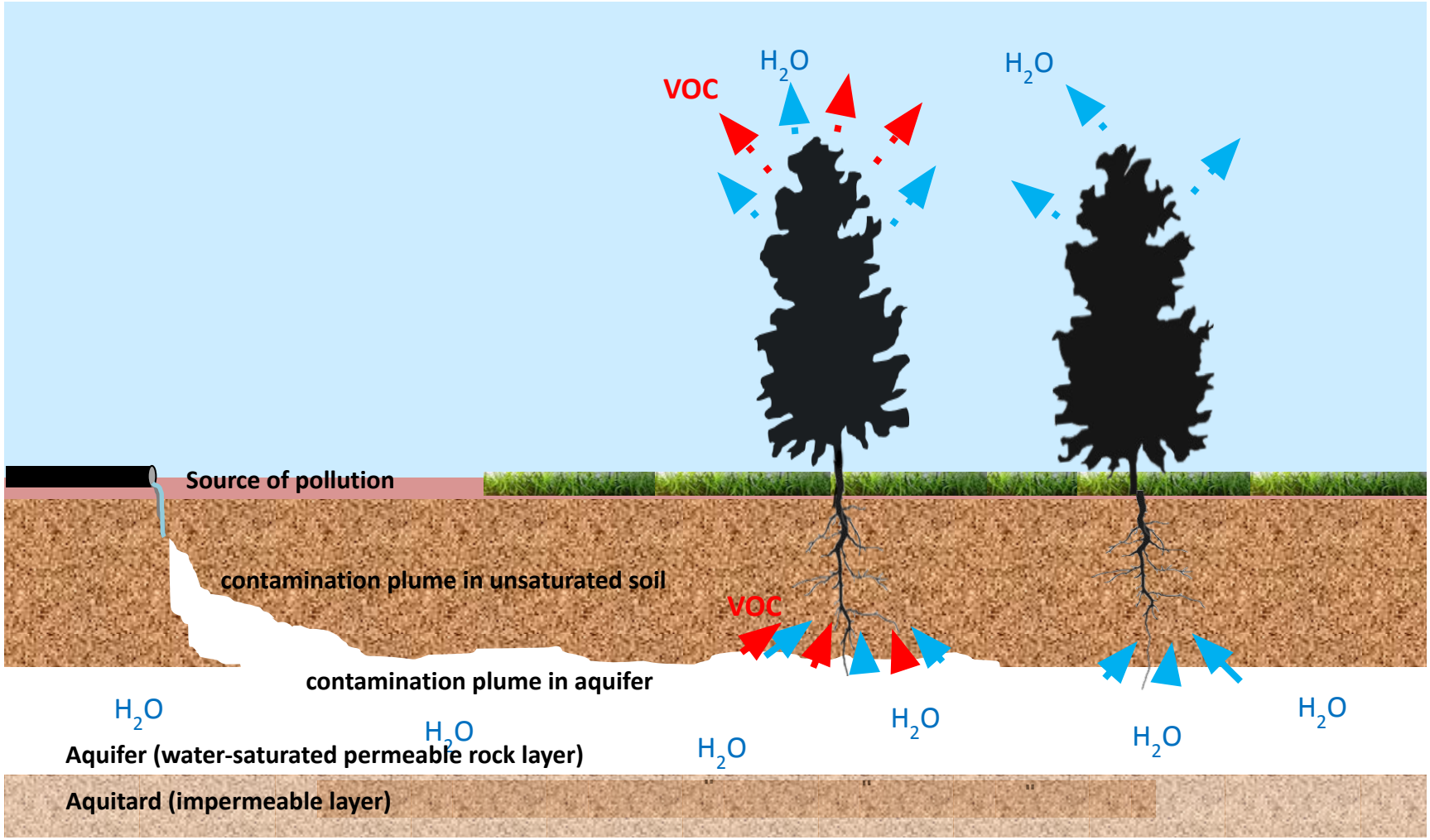
ENVIRONMENTAL CHEMISTRY
DEPARTMENT, CXI

Technical University of Liberec, Czechia

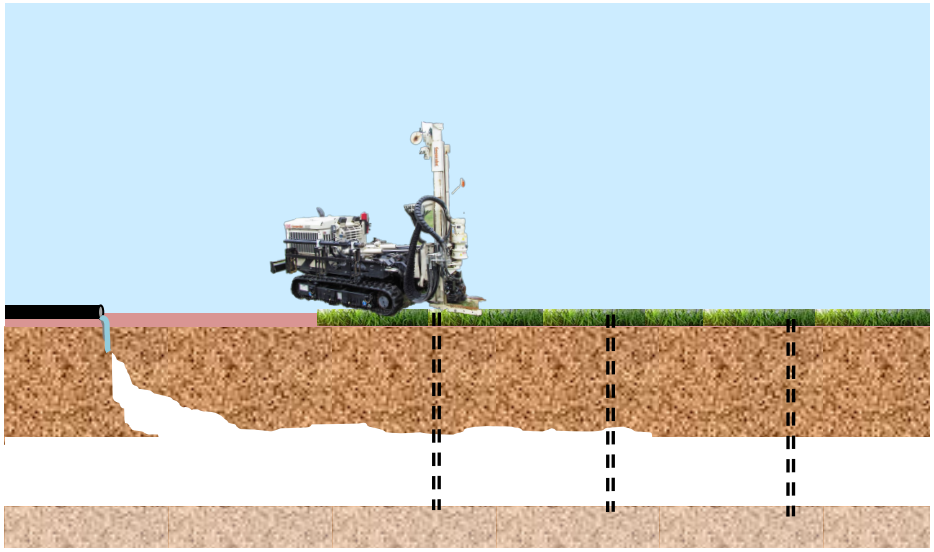
14th International HCH and Pesticides Forum

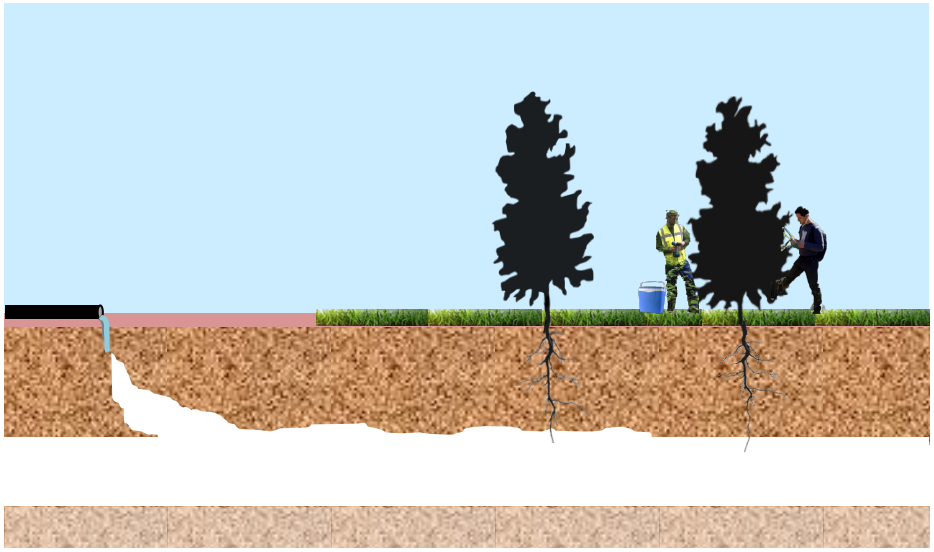
GROUNDWATER HCH INDICATION VIA PHYTOSCREENING OF TREES

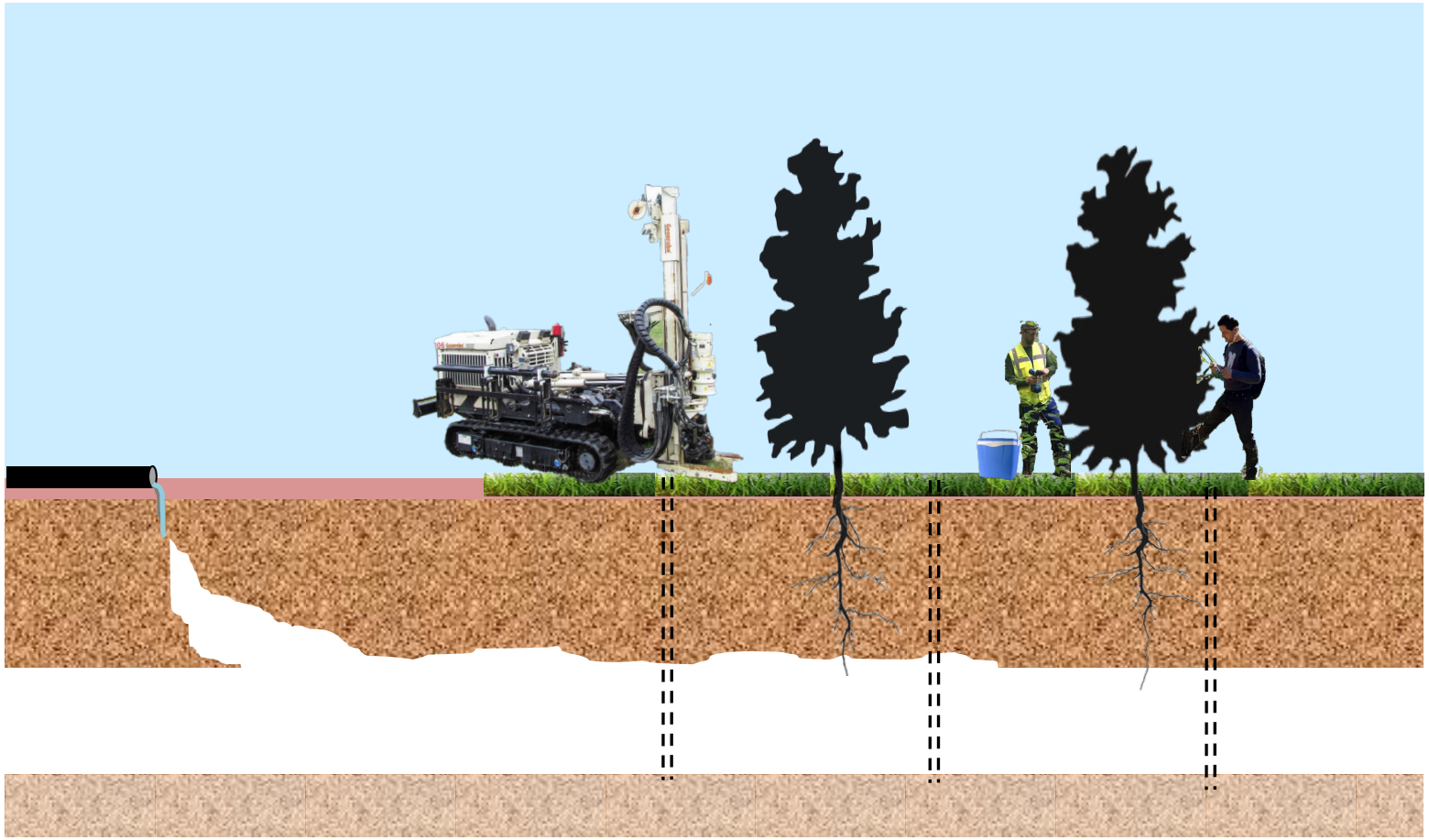
Stanislava Vrchovecká, Tereza Sázavská, Vojtěch Antoš, Pavel Hrabák


VOC
H2O
H2O
Source of pollution
contamination plume in unsaturated soil
VOC
contamination plume in aquifer
H2O
H2O
H2O
H2O
H2O
H2O
Aquifer (water-saturated permeable rock layer)
Aquitard (impermeable layer)

GROUNDWATER SURVEY APPROACHES







GROUNDWATER SURVEY APPROACHES

Standard hydrogeological survey by penetration probe and MIP

Phytoscreening

GROUNDWATER SURVEY APPROACHES

Standard hydrogeological survey by penetration probe and MIP

Phytoscreening

NO VEGETATION – NO PHYTOSCREENING

Standard hydrogeological survey by penetration probe and MIP

Phytoscreening

PRESENTATION OVERVIEW

- Phytoscreening history (of volatile pollutants)
- Tree uptake of HCH
- Czech and Polish HCH sites
- HCH isomer-specific phytoaccumulation
- HCH distribution in tree trunks
- Genotype differences of HCH uptake by alders
- Analytical approaches to HCH in tree biomass
- Birch sap monitoring

PHYTOSCREENING HISTORY

- **J. G. Burken** a J. L. Schnoor, „Predictive Relationships for Uptake of Organic Contaminants by Hybrid Poplar Trees", *Environ. Sci. Technol.*, roč. 32, č. 21, s. 3379–3385, lis. 1998. (700 citations)
- **D. A. Vroblesky**, C. T. Nietch, a J. T. Morris, „Chlorinated Ethenes from Groundwater in Tree Trunks", *Environ. Sci. Technol.*, roč. 33, č. 3, s. 510–515, úno. 1999 (164 citations)
- **A. Sorek** *et al.*, „“Phytoscreening”: The Use of Trees for Discovering Subsurface Contamination by VOCs", *Environ. Sci. Technol.*, roč. 42, č. 2, s. 536–542, led. 2008 (82 citations)
- More than 20 other publications on VOC phytoscreening (**M. Limmer**, **S. Trap**, …)

SCIENTIFIC STUDIES ON VOC PHYTOSCREENING

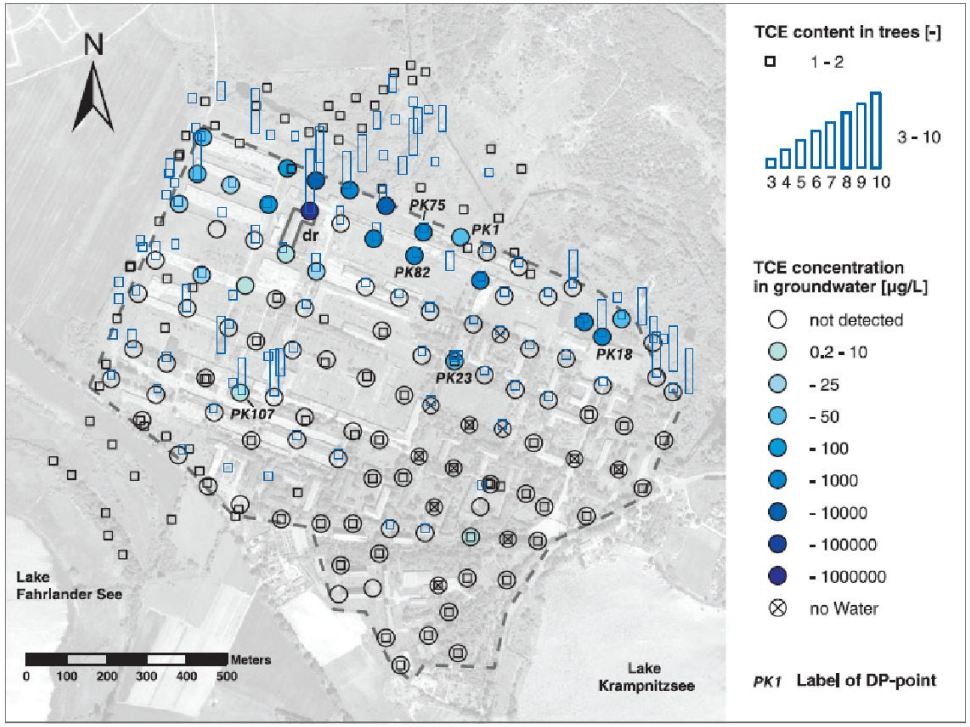
PCE/TCE case: deep knowledge of tree uptake (24 impacted publications – keyword phytoscreening):

- Environmental Science & Technology, IF 7,25: 7 pc (2008 – 2014)
- Chemosphere, IF 4,5: 2 pc (2014, 2017)
- Environmental Science and Pollution Research, IF 2,9: 2 pc (2013, 2016)
- Science of the Total Environment, IF 4,9: 2 pc (2017, 2018)
- Environmental Science – Water Research & Technology, IF 3,6: 1 pc (2015)

Q1 + Q2 = 14 pc

- Groundwater Monitoring and Remediation, IF 1,4: 3 pc (2014 - 2018)
- International Journal of Phytoremediation, IF 2,0: 4 pc (2011 - 2015)
- Environmental Monitoring and Assessment, IF 2,0: 1 pc (2016)
- Journal of Environmental Engineering, IF 1.5: 1 pc (2013)

Q3 + Q4 = 9 pc



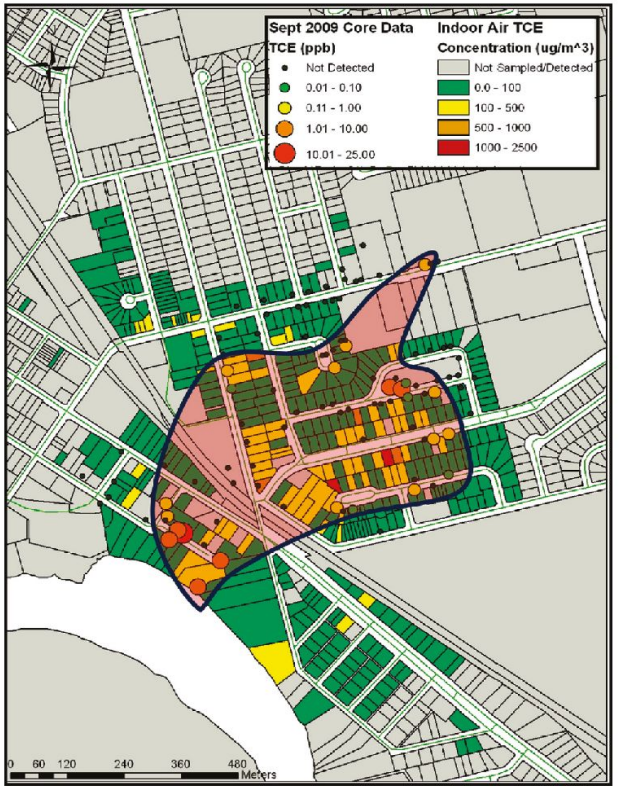


Figure 2. Phytoscreening data via tree cores and relation of measured indoor concentrations from Cambridge Ontario, Bishop Street Site. Trees sampled were of widely ranging species, age, and size. Shaded area outlines the tree cores positive for TCE and covers the majority of homes with indoor concentrations above action levels. (Figure prepared by Matt Limmer at Missouri S&T and Camilo Martinez with the Ontario Ministry of the Environment).

Rein at all, 2015, *Groundwater Monitoring & Remediation* 35 (4): 45–56.

Matt Limmer and Camilo Martinez

HCH - tree bioaccumulation

- ***Populus sp.*:** R. Bernini *et al.*, „Dendrochemical investigation on hexachlorocyclohexane isomers (HCHs) in poplars by an integrated study of micro-Fourier transform infrared spectroscopy and gas chromatography", *Trees*, roč. 30, č. 4, s. 1455–1463, srp. 2016.
- **Juglans sp.:** S. Battisti *et al.*, „Measurements of β and α hexachlorocyclohexane in Juglans regia and Prunus spinosa trees in a contaminated area, central Italy", *Environ Sci Pollut Res Int*, roč. 24, č. 26, s. 20876–20882, 2017.
- ***Prunus*** sp., ***Robinia*** sp., ***Crataegus*** sp.: Liu et al., Uptake and metabolization of HCH Isomers in Trees Examined over an Annual Growth Period by Compound-Specific Isotope Analysis and Enantiomer Fractionation. *Environ. Sci. Technol*. 56, 10120-10130 (2022)

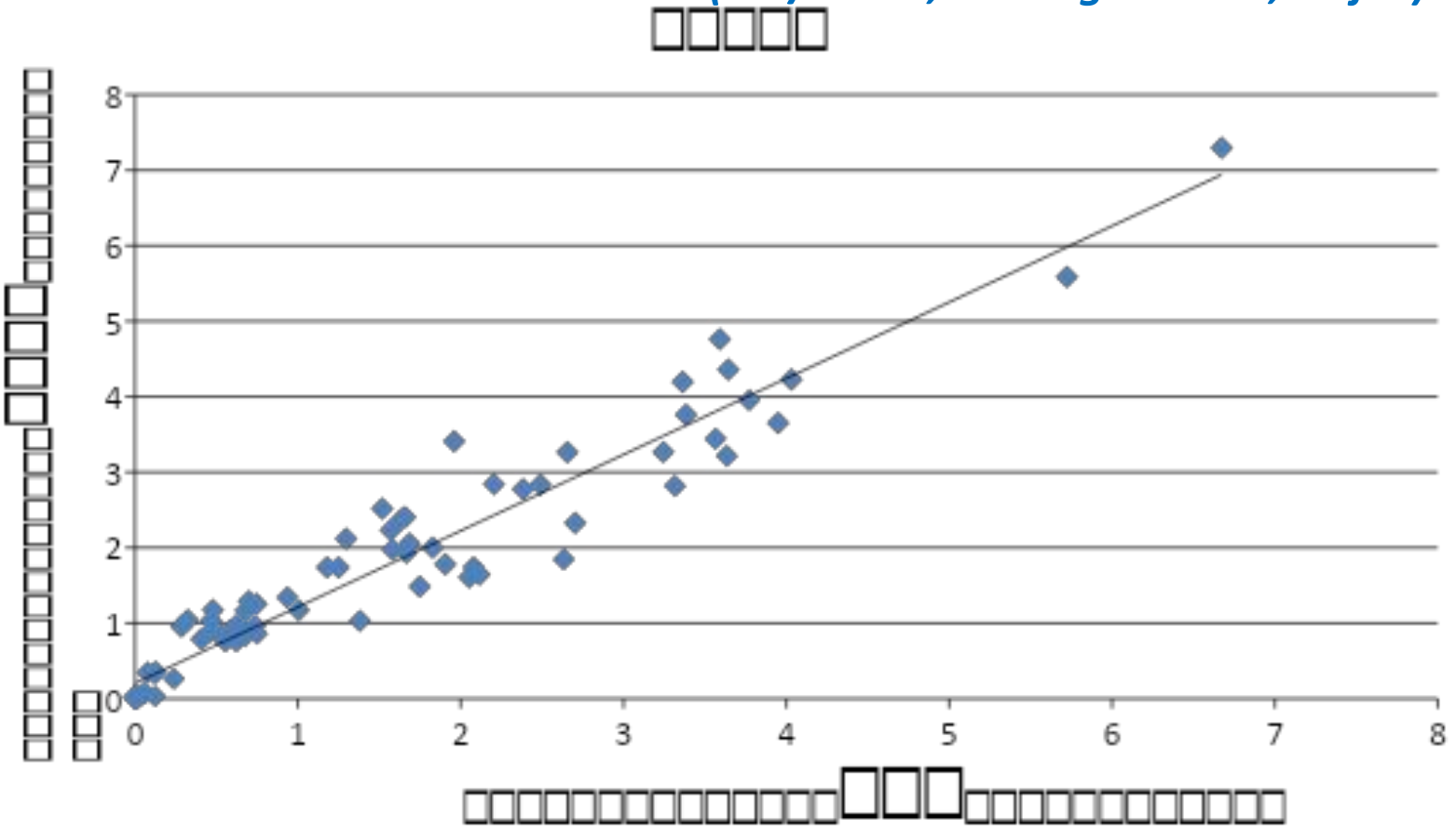
HCH – shrubs bioaccumulation

- ***Cynara and Erica sp.:*** Calvelo Pereira, R. et. all, 2008. Distribution pathways of hexachlorocyclohexane isomers in a soil-plant-air system. A case study with Cynara scolymus L. and Erica sp. plants grown in a contaminated site. Environmental Pollution 155, 350–358.
- ***Cytisus striatus*:** Becerra-Castro, C. et all, 2013. Phytoremediation of hexachlorocyclohexane (HCH)-contaminated soils using Cytisus striatus and bacterial inoculants in soils with distinct organic matter content. Environmental Pollution 178, 202–210.
- **Different species:** H. E. Balázs *et al.*, „HCH phytoremediation potential of native plant species from a contaminated urban site in Turda, Romania", *J. Environ. Manage.*, roč. 223, s. 286–296, 2018.

HCH PHYTOSCREENING AT 2 SITES IN CZ & PL

- Field and lab methods **verification** (GC-MS, LOD < 0.01 µg.g_{dw}^{-1})
- **Confirmation**: HCH presence in tree biomass in HCH-contaminated areas
- Checking the fit with known **gradients** (Ostrovský creek profiling)
- **Multispecies aerial phytoscreening** of HCH in tree biomass (Hájek, Jaworzno) + match with groundwater data
- Single species phytoscreening + match with groundwater data
- HCH **distribution** within the tree – harvesting and subsampling
  - **Age, height, health status, seasonality, azimuthal** effects
- Lab – **exposure** experiments (isomer specificity, metabolites,…)
- **Birch sap** monitoring

Extraction methods *(LLE/SPME, Alnus glutinosa, Hájek)*



Extraction options in HCH phytoscreening

Solvent extraction

- Classical extraction
- approx 0,5-1 g of sample
- + 10 ml of [illegible] 1:1
- Shaki[illegible]
- Extra[illegible]
- Ad[illegible]dards (D[illegible]HClB)
- Classical calibration
- Liquid injection into GC/MSMS

EXHAUSTIVE

SPME

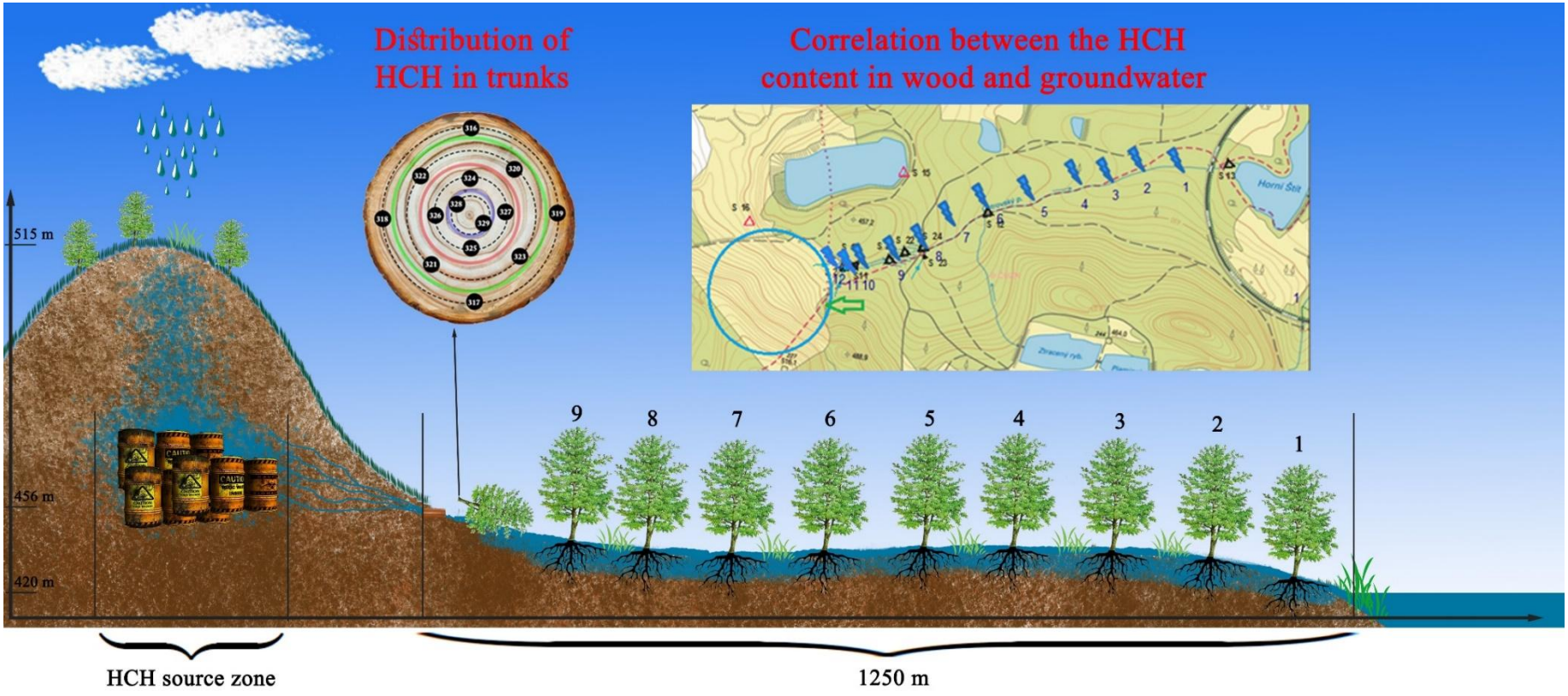
- Green extraction
- approx 0,5-1 g of sample
- +10 ml of tap w[illegible]
- Shaking ov[illegible]
- Addition [illegible]s (D6 γ-HC[illegible]
- Matr[illegible], reverse process to extrac[illegible]n = s[illegible]erence, clean matrix needed)
- Thermal desorption injection into GC/MSMS

SELECTIVE

5 HCH isomers, 13 ClB analogues with LOQ 0.01 µg.g_{dw}^{-1}

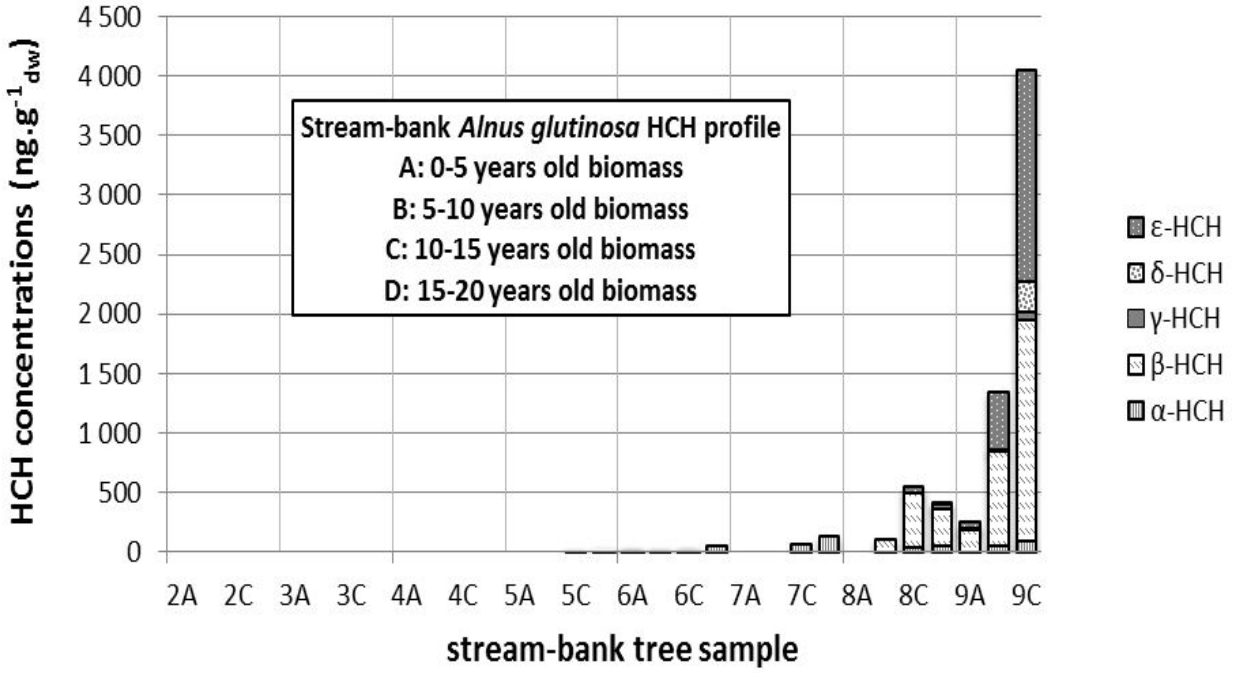
(+weight-out and dry mass correction)

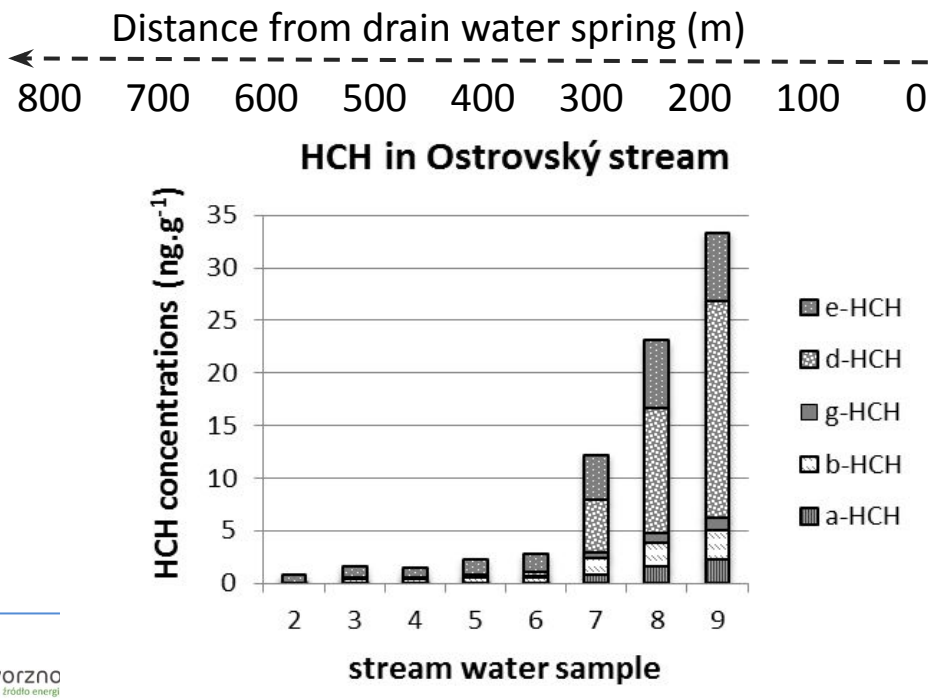
Ostrovský creek profiling



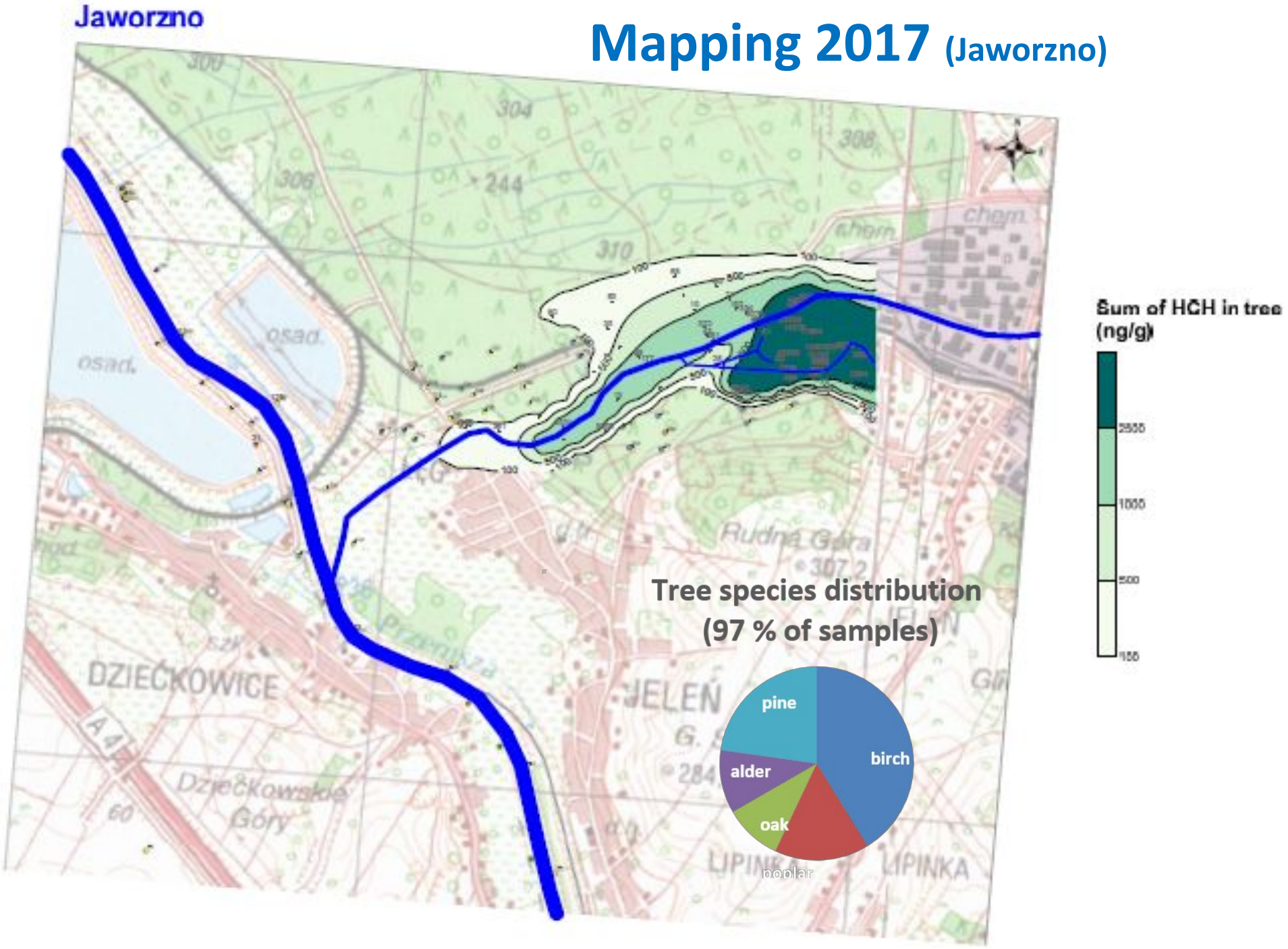
Stream Profiling

(Hájek)

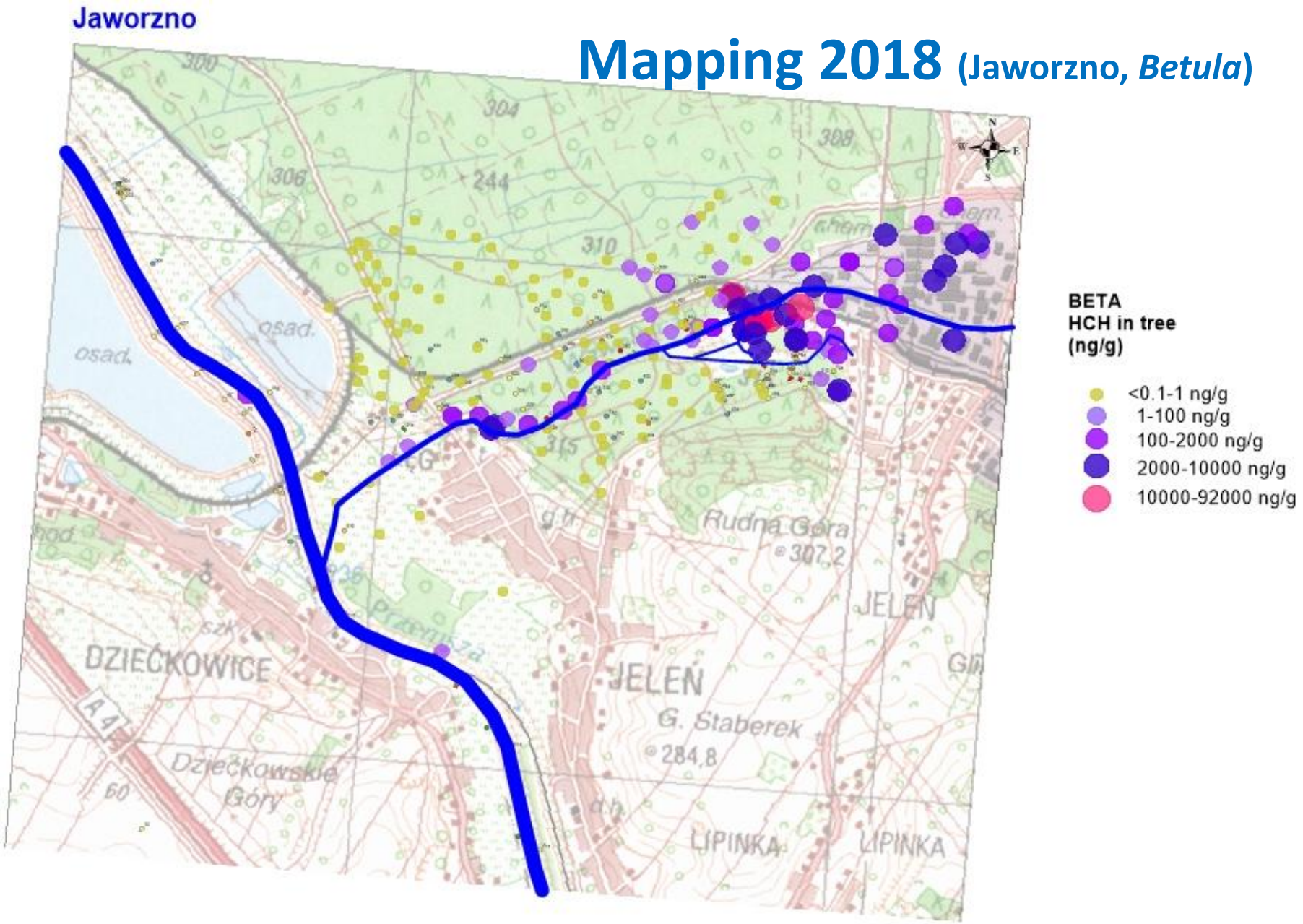




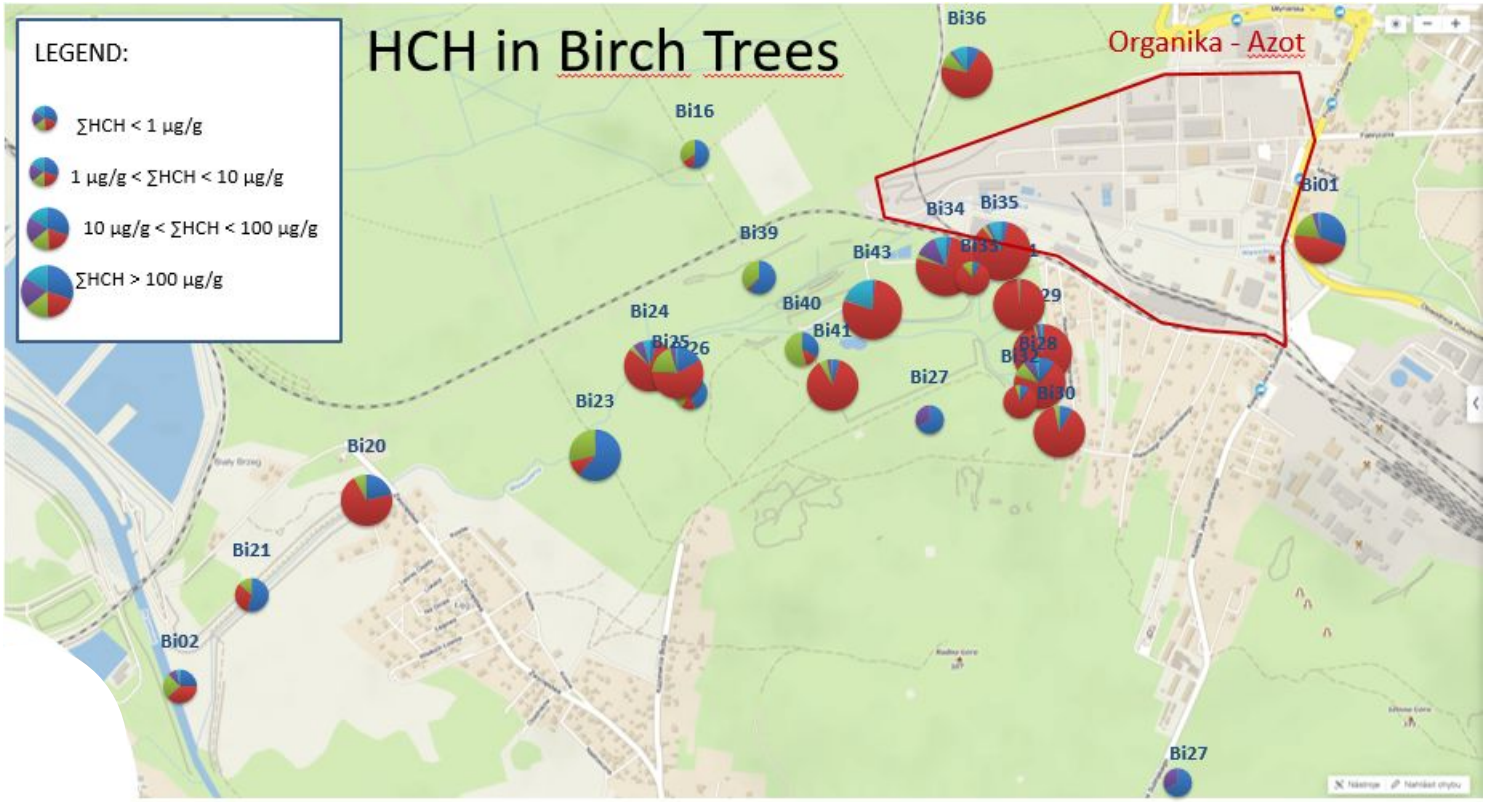
Mapping 2017 (Jaworzno)

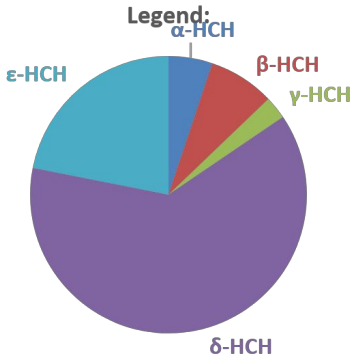


Mapping 2018 (Jaworzno, *Betula*)



Mapping 2020 (Jaworzno, *Betula*)

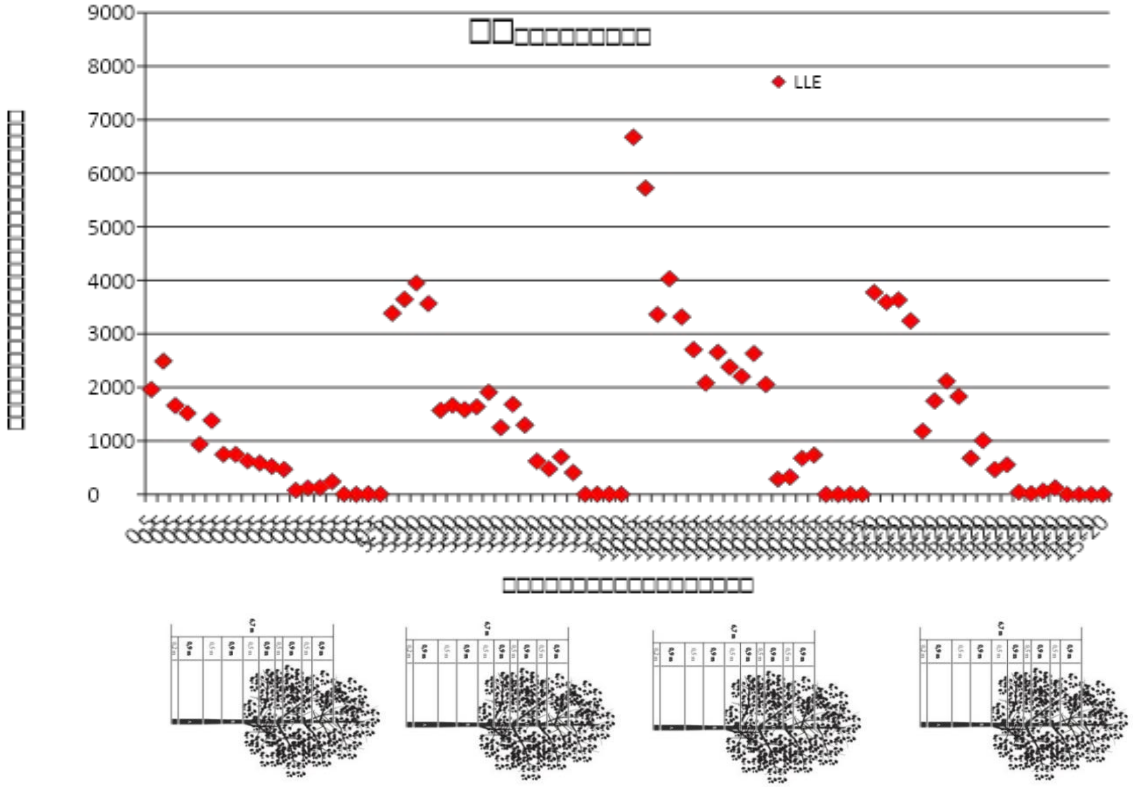


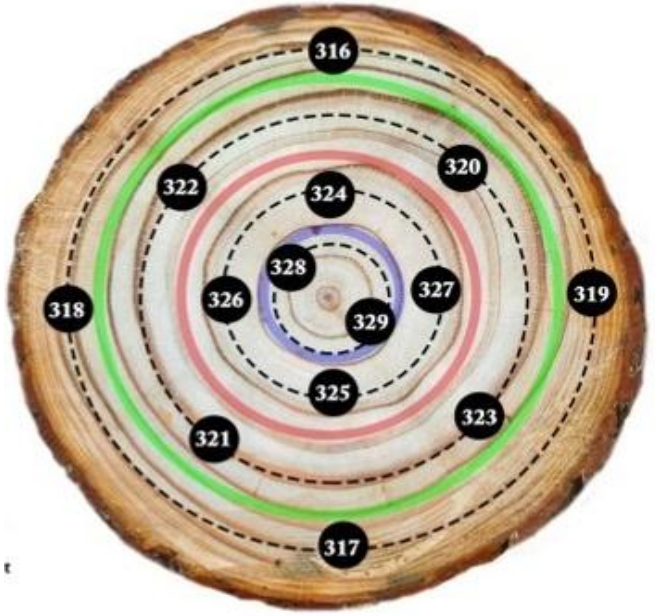



125A

Age & height dependence

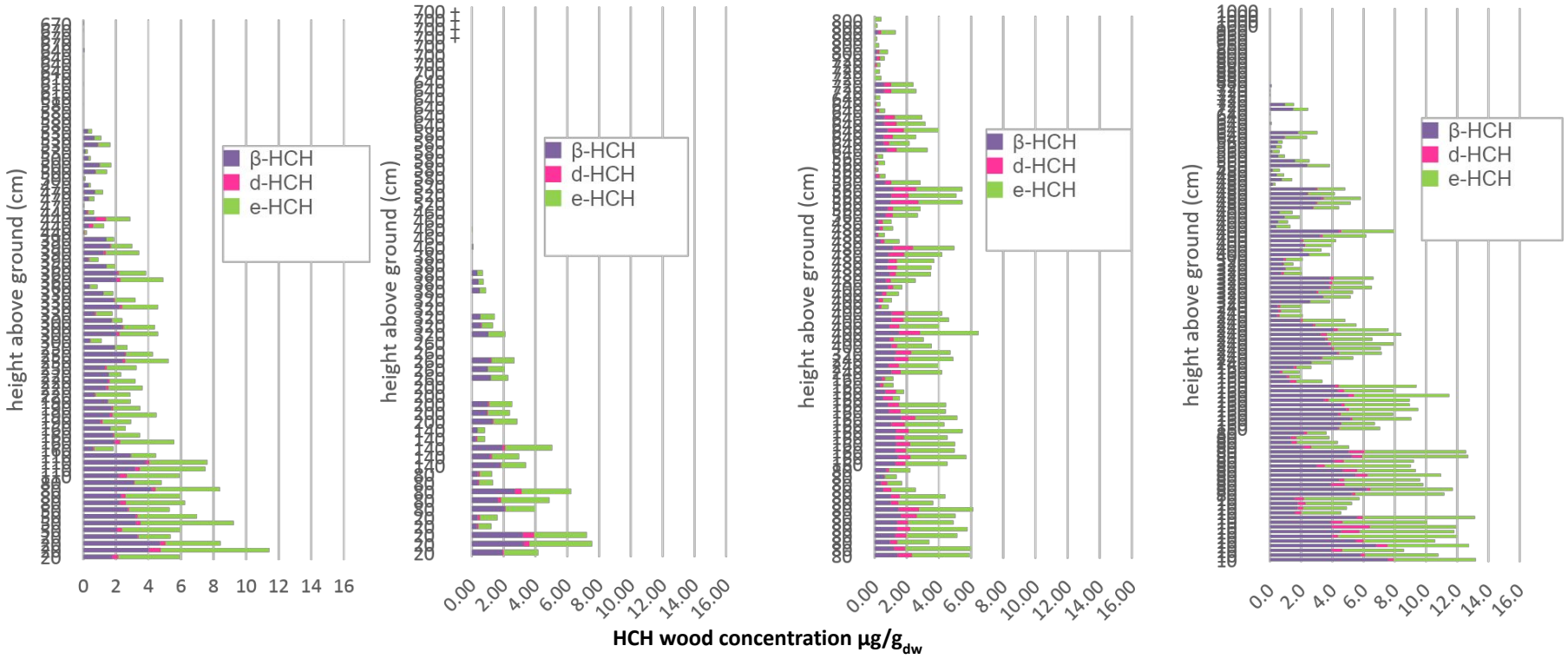
(Alnus glutinosa, Hájek)



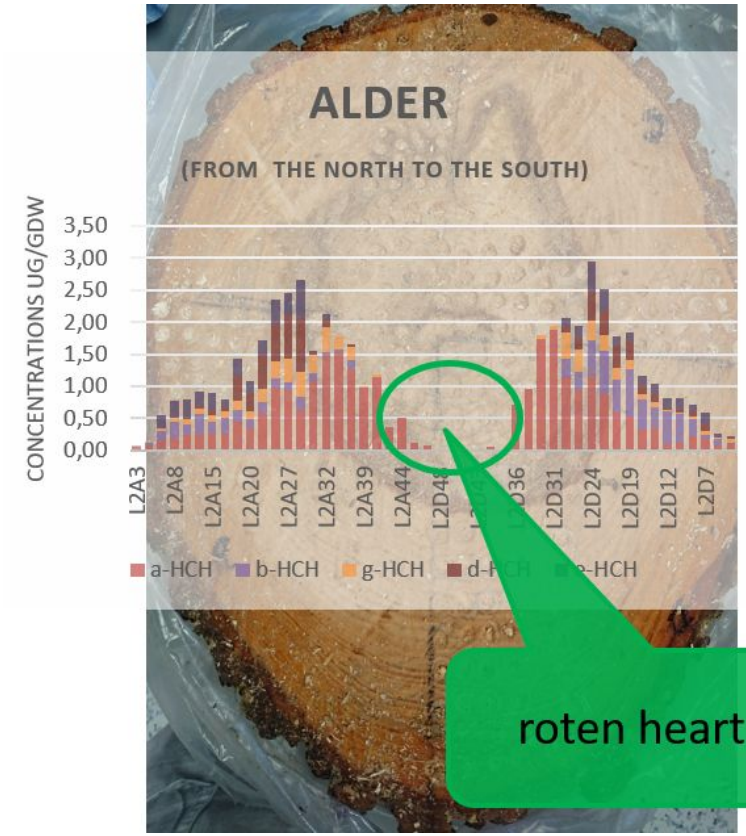


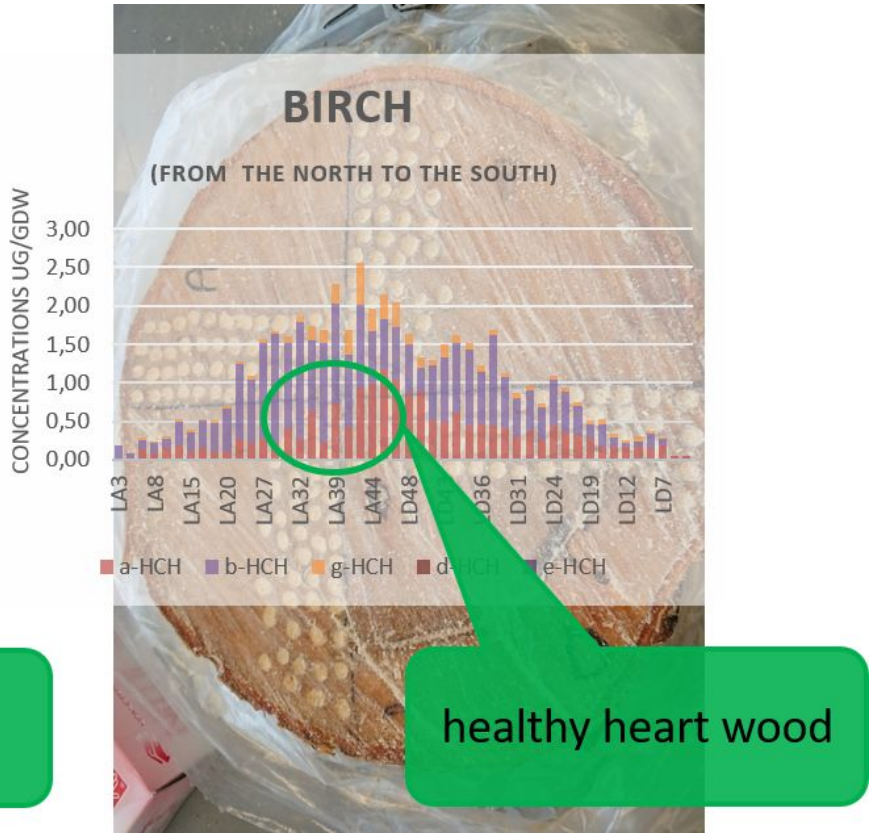
Seasonality study *(Alnus glutinosa, Hájek)*

July 2015, **LLE** | October 2015, **LLE** | March 2016, **LLE** | July 2016, **LLE**

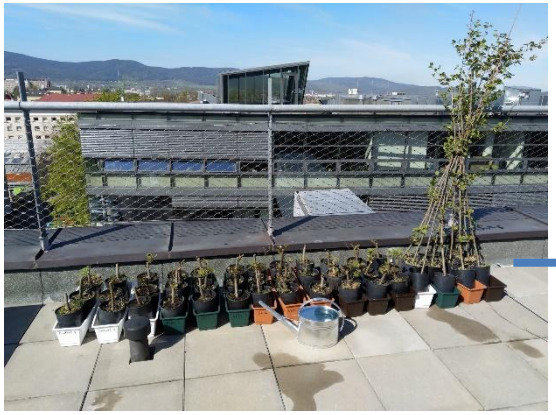


Health status

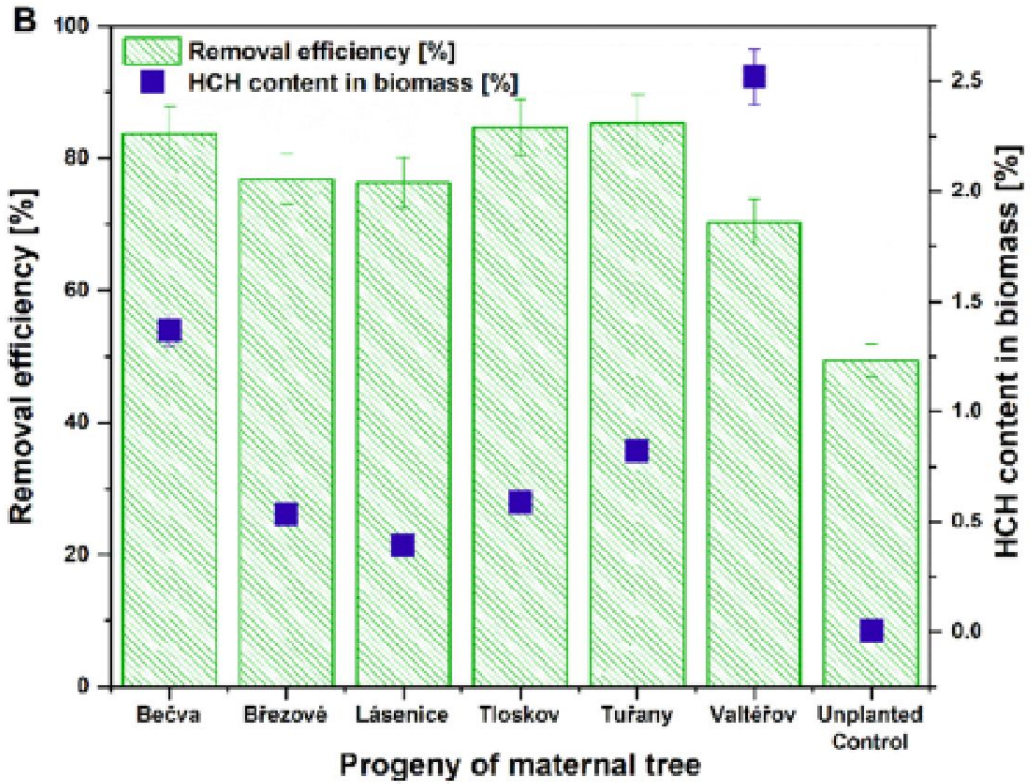




Seedlings exposure to HCH



Seedlings exposure to HCH



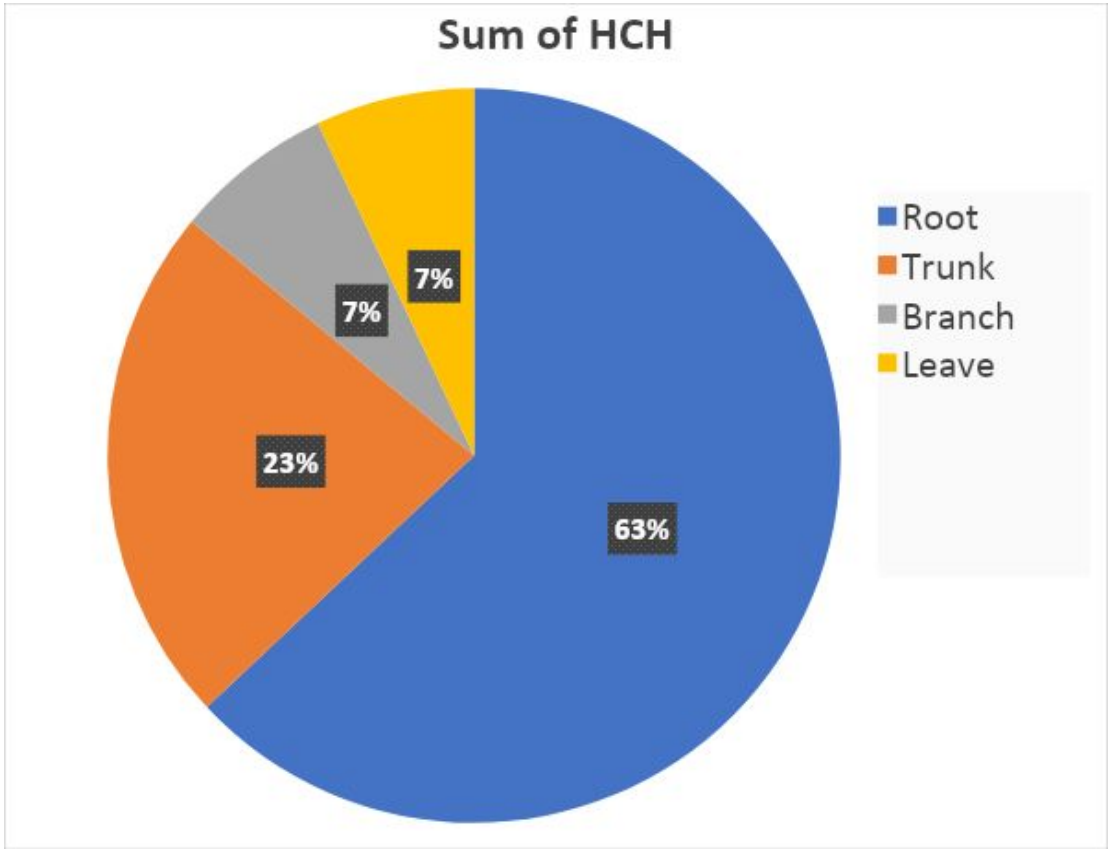
Košková, S., Štochlová, P., Novotná, K., Amirbekov, A. & Hrabák, P. Influence of delta-hexachlorocyclohexane (δ-HCH) to Phytophthora ×alni resistant Alnus glutinosa genotypes − Evaluation of physiological parameters and remediation potential. *Ecotoxicology and Environmental Safety* **247**, 114235 (2022).

Seedlings exposure to HCH

Preliminary result from AU experiment (to be published soon…)

- Experimental design in Carlos Arias presentation…
- Trans-isomerization – YES (δ-HCH in stock solution → all HCH isomers in plant!,)
- Uniform uptake – YES (no difference among α-HCH, β-HCH, γ-HCH and δ-HCH uptake when technical HCH mix was dosed)

Seedling exposure *(Liberec, CxI, Alnus glutinosa)*

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Screening for metabolites

- Non-target analysis with HPLC-qTOF_HRMS
- Primary metabolites of HCH
  - Chlorobenzenes (confirmed) ✓
  - Chlorophenols – conjugated with glucose or malonate – confirmed ✓
- Plant secondary metabolome
  - Influence confirmed (chlorgenic acid, neochlorogenic acid, ferulic acid, flavonoids, triterpenoids, tannins, dihydrochalcones, phenolic diterpenes) ✓

Conclusions

- Tree indicate groundwater HCH contamination, phytoscreening of HCH can be used for mapping (preferentially with one species dominating the site)
- Isomeric pattern is changed – selective uptake or trans-isomerisation?
- Coniferous trees are much less sensitive than deciduous trees
- SPME protocol can be used as a green analytical technique
- HCH distribution in Alnus glutinosa was well described (age, height, seasonality dependence), spring and summer seasons should be preferred for phytoscreening
- Azimuthal HCH phytoscreening did not bring a match with known gradients
- Major part of HCH dwells in roots of plants
- Tree presence leads to faster soil remediation from HCH load
- Birch sap is not a very sensitive matrix, solid tree biomass is more suitable for HCH phytoscreening, moreover – it is only available in March/April

Acknowledgements

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Contact information

https://cxi.tul.cz/lifepopwat/home

pavel.hrabak@tul.cz, stanislava.vrchovecka@tul.cz

+42 774 844 038