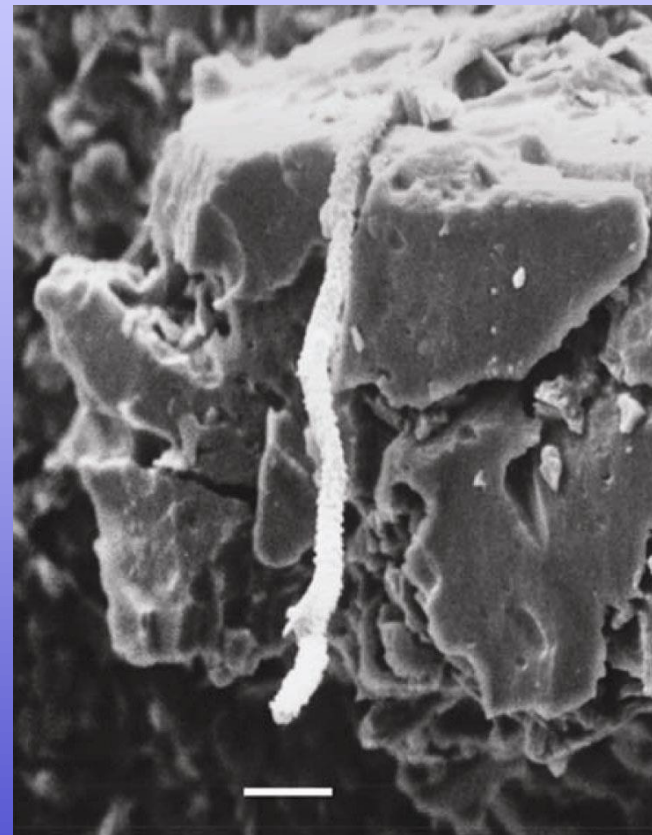
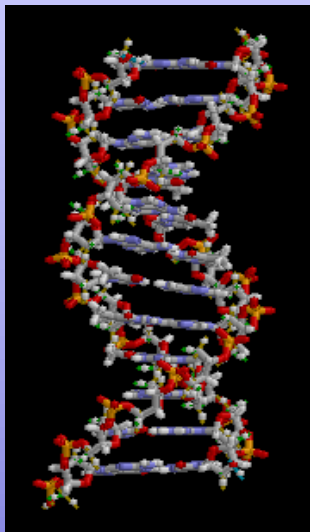


GEOMYKOLOGIE VI.

(houby a arzén)



25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96
43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60
75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)



RNDr. Jan Borovička, Ph.D.

Ústav jaderné fyziky AV ČR / Geologický ústav AV ČR

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1	H Vodík 1.00794	Mo Molybden 95.96 2-8-18-13-1				Nekovy	Halogeny					He Helium 4.002602						
2	Li Lithium 6.941	Be Berylium 9.012182	Alkalické kovy				Přechodné kovy					B Bor 10.811	C Uhlík 12.0107	N Dusík 14.0067	O Kyslík 15.9994	F Fluor 18.9984032	Ne Neon 20.1797	
3	Na Sodík 22.98976928	Mg Hořčík 24.3050	Kovy alkalických zemin				Kovy					Al Hliník 26.9815386	Si Křemík 28.0855	P Fosfor 30.973762	S Síra 32.065	Cl Chlor 35.453	Ar Argon 39.948	
4	K Draslík 39.0983	Ca Vápník 40.078	Sc Skandium 44.955912	Ti Titan 47.867	V Vanad 50.9415	Cr Chrom 51.9961	Mn Mangan 54.938045	Fe Železo 55.845	Co Kobalt 58.933195	Ni Nikl 58.6934	Cu Měď 63.546	Zn Zinek 65.38	Ga Galium 69.723	Ge Germanium 72.64	As Arsen 74.92160	Se Selen 78.96	Br Brom 79.904	Kr Krypton 83.798
5	Rb Rubidium 85.4678	Sr Stroncium 87.62	Y Ytrium 88.90585	Zr Zirkonium 91.224	Nb Niob 92.90638	Mo Molybden 95.96	Tc Technecium (97.9072)	Ru Ruthenium 101.07	Rh Rhodium 102.90550	Pd Paladium 106.42	Ag Stříbro 107.8682	Cd Kadmium 112.411	In Indium 114.818	Sn Cín 118.710	Sb Antimon 121.760	Te Telur 127.60	I Jod 126.90447	Xe Xenon 131.293
6	Cs Cesium 132.9054519	Ba Barium 137.327	La-Lu	Hf Hafnium 178.49	Ta Tantal 180.94788	W Wolfram 183.84	Re Rhenium 186.207	Os Osmium 190.23	Ir Iridium 192.217	Pt Platina 195.084	Au Zlato 196.966569	Hg Rtuť 200.59	Tl Thalium 204.3833	Pb Olovo 207.2	Bi Bismut 208.98040	Po Polonium (208.9824)	At Astat (209.9871)	Rn Radon (222.0176)
7	Fr Francium (223)	Ra Radium (226)	Ac-Lr	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (266)	Bh Bohrium (264)	Hs Hassium (277)	Mt Meitnerium (268)	Ds Darmstadtium (271)	Rg Rentgenium (272)	Cn Copernicium (285)	Uut Ununtrium (284)	Fl Flerovium (289)	Uup Ununpentium (288)	Lv Livermorium (292)	Uus Ununseptium (294)	Uuo Ununoctium (294)

U prvků s nestabilními isotopy je uvedena molová hmotnost nejdéle žijícího isotopu v zátvorkách

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La Lanthan 138.90547	Ce Cer 140.116	Pr Praseodym 140.90765	Nd Neodym 144.242	Pm Promethium (145)	Sm Samarium 150.36	Eu Europium 151.964	Gd Gadolinium 157.25	Tb Terbium 158.92535	Dy Dysprosium 162.5	Ho Holmium 164.93032	Er Erbium 167.259	Tm Thulium 168.93421	Yb Ytterbium 173.054	Lu Lutecium 174.9668
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac Aktinium (227)	Th Thorium 232.03806	Pa Protaktinium 231.03588	U Uran 238.02891	Np Neptunium (237)	Pu Plutonium (244)	Am Americium (243)	Cm Curium (247)	Bk Berkelium (247)	Cf Californium (251)	Es Einsteinium (252)	Fm Fermium (257)	Md Mendelevium (258)	No Nobelium (259)	Lr Lawrencium (262)

Arzén je prvek patřící mezi POLOKOVY neboli METALOIDY.

Problematická skupina prvků kombinující vlastnosti kovů (pevnost a lesk) a nekovů (vyšší elektronegativita, tj. vyšší schopnost přitahovat vazebné elektrony)

ARZÉN / ARSEN

Chemická značka As, latinsky *Arsenicum*.

Chalkofilní prvek, polokov (metaloid).

V přírodě monoizotopní prvek (^{75}As , 100% zastoupení)

Lidstvu známý tisíce let – zejména díky své toxicitě.

Problémy při zpracování rud: arzén se přidával k vylepšení tvrdosti mědi v oblastech, kde nebyl k dispozici cín. Vznik toxického těkavého As_2O_3 .

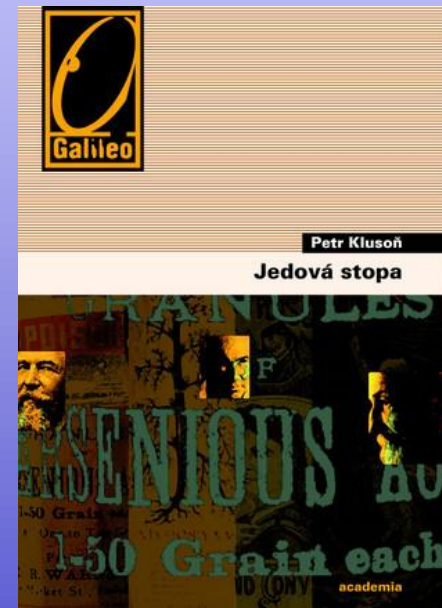
Řecký bůh kovářství Hefaistos je často ošklivý a kulhá, že by důsledek chronické otravy arzánem?



Z historie travičství

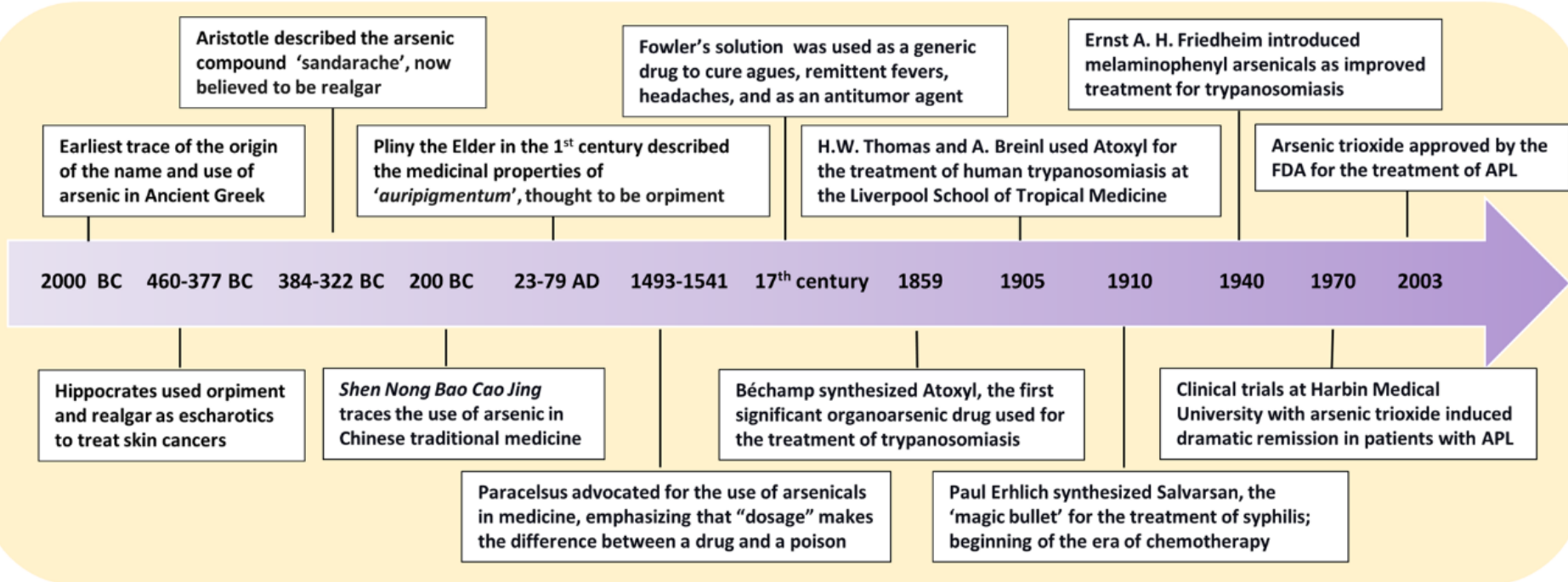
Oxidu arsenitému (As_2O_3) staří Řekové říkali arsenikon, což v jejich jazyce znamenalo mužný nebo silný. Z této substance se v průběhu staletí stal jednoznačně nejzneužívanější jed lidské historie (otrušík, utrejch).

- nenápadnost (bílý prášek bez chuti rozpustný ve vodě i alkoholu)
- všeobecná dostupnost
- jednoduchá příprava
- smrtelná dávka pro člověka ~120 mg (orálně)
- s lékařskou pomocí lze přežít i 9 000 mg¹



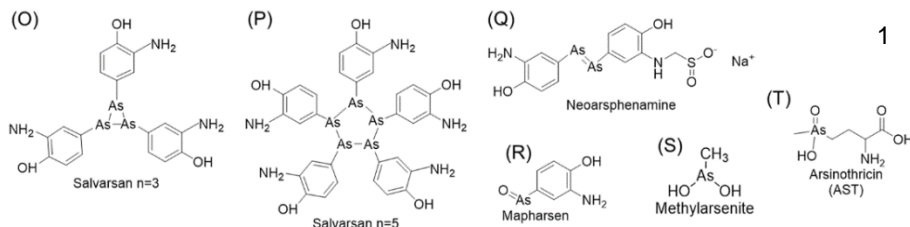
V období 1820–1860 bylo v Anglii, Německu, Španělsku a Francii na 1000 kriminálních případů otrav, 350 až 500 spojených přímo s oxidem arsenitým.

Využití arzénu v medicíně



Využití v medicíně již od roku 2000 př.n.l., prakticky skončilo objevem antibiotik, ale existují i protinádorové účinky sloučen arzénu.

Antibiotics/antimicrobials



Arsphenamine, also known as Salvarsan or compound 606

¹Paul et al. (2023) Biometals (2023) 36:283–301.

Arzén jako biogenní prvek?

Biogenní prvky jsou takové, které jsou nezbytné pro život.

FOSFOR: vyskytuje se v kostech, zubech, v ATP (adenosintrifosfát) a v nukleových kyselinách (DNA, RNA).

ARZÉN má některé vlastnosti a chemické chování společné s fosforem.

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Nov. 29, 2010

Cathy Weselby
Ames Research Center, Moffett Field, Calif.
650-604-2791
cathy.weselby@nasa.gov

MEDIA ADVISORY : M10-167

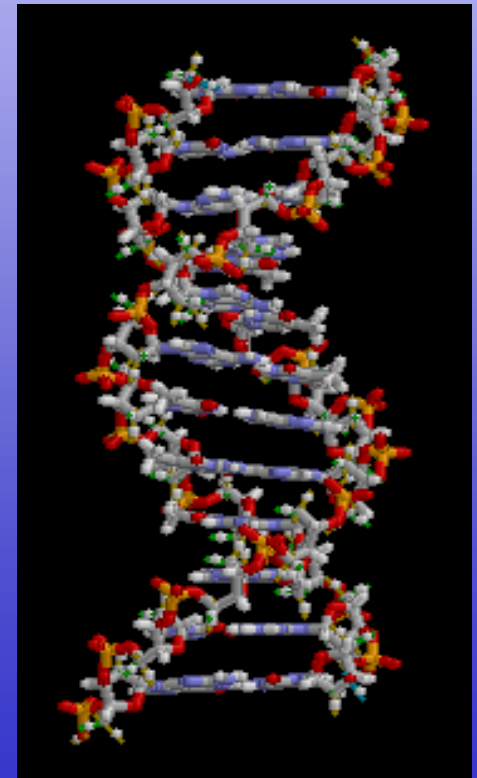
NASA Sets News Conference on Astrobiology Discovery; Science Journal Has Embargoed Details Until 2 p.m. EST On Dec. 2

WASHINGTON -- NASA will hold a news conference at 2 p.m. EST on Thursday, Dec. 2, to discuss an astrobiology finding that will impact the search for evidence of extraterrestrial life. Astrobiology is the study of the origin, evolution, distribution and future of life in the universe.

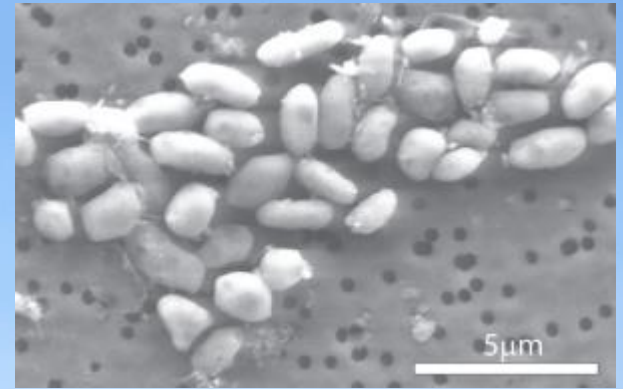
The news conference will be held at the NASA Headquarters auditorium at 300 E St. SW, in Washington. It will be broadcast live on NASA Television and streamed on the agency's website at <http://www.nasa.gov>.

Participants are:

- Mary Voytek, director, Astrobiology Program, NASA Headquarters, Washington
- Felisa Wolfe-Simon, NASA astrobiology research fellow, U.S. Geological Survey, Menlo Park, Calif.
- Pamela Conrad, astrobiologist, NASA's Goddard Space Flight Center, Greenbelt, Md.
- Steven Benner, distinguished fellow, Foundation for Applied Molecular Evolution, Gainesville, Fla.
- James Elser, professor, Arizona State University, Tempe



Jezero Mono CA, USA



GFAJ-1 bakterie mohou žít při vysokých koncentracích As v prostředí

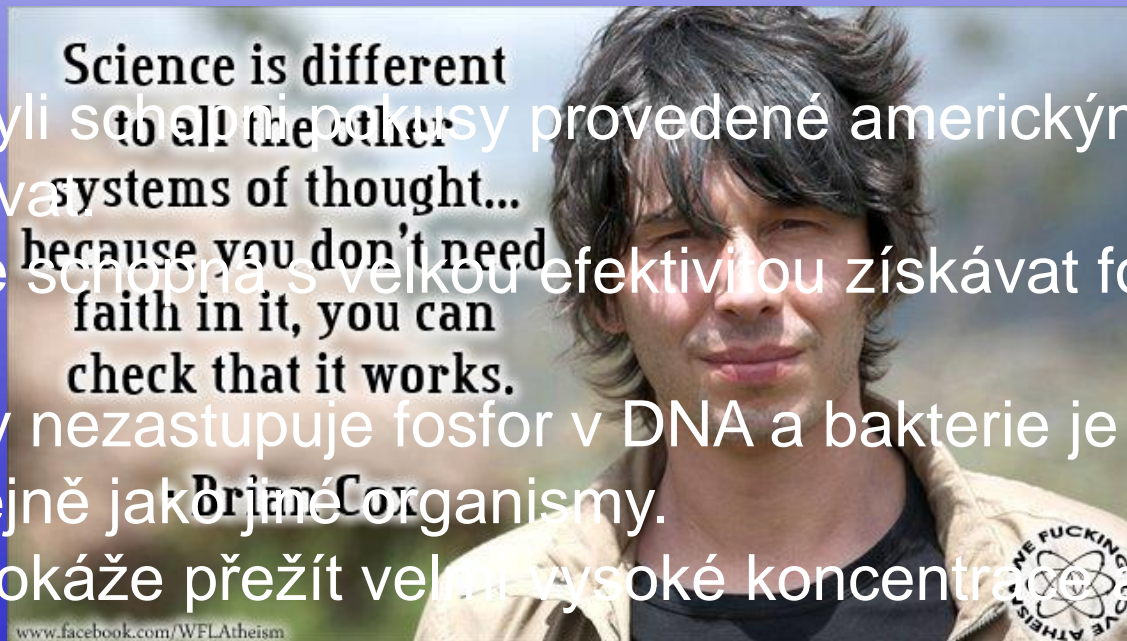


Arzén jako biogenní prvek?

The screenshot shows the Science journal website. The main article is titled "A Bacterium That Can Grow by Using Arsenic Instead of Phosphorus" by Felisa Wolfe-Simon^{1,2*}, Jodi Switzer Blum², Thomas R. Kulp², Gwyneth W. Gordon³, Shelley E. Hoefft², Jennifer Pett-Ri... The article is dated 03 Jun 2011, Vol. 332, Issue 6034, pp. 1163-1166, DOI: 10.1126/science.1197258. The website header includes navigation links for Home, News, Journals, Topics, and Careers, and a search bar.

Bakterie GFAJ-1 dokáže využít arzén jako prvek zastupující fosfor v DNA.

- Vědci nebyli schopni pokusy provedené americkým týmem reprodukovat v jiných systémech myšlení...
- Bakterie je schopna s velkou efektivitou získávat fosfor z prostředí.
- Arzén tedy nezastupuje fosfor v DNA a bakterie je na fosforu závislá stejně jako jiné organismy.
- Bakterie dokáže přežít velmi vysoké koncentrace arzénu.



Česko – země arzénu zaslíbená

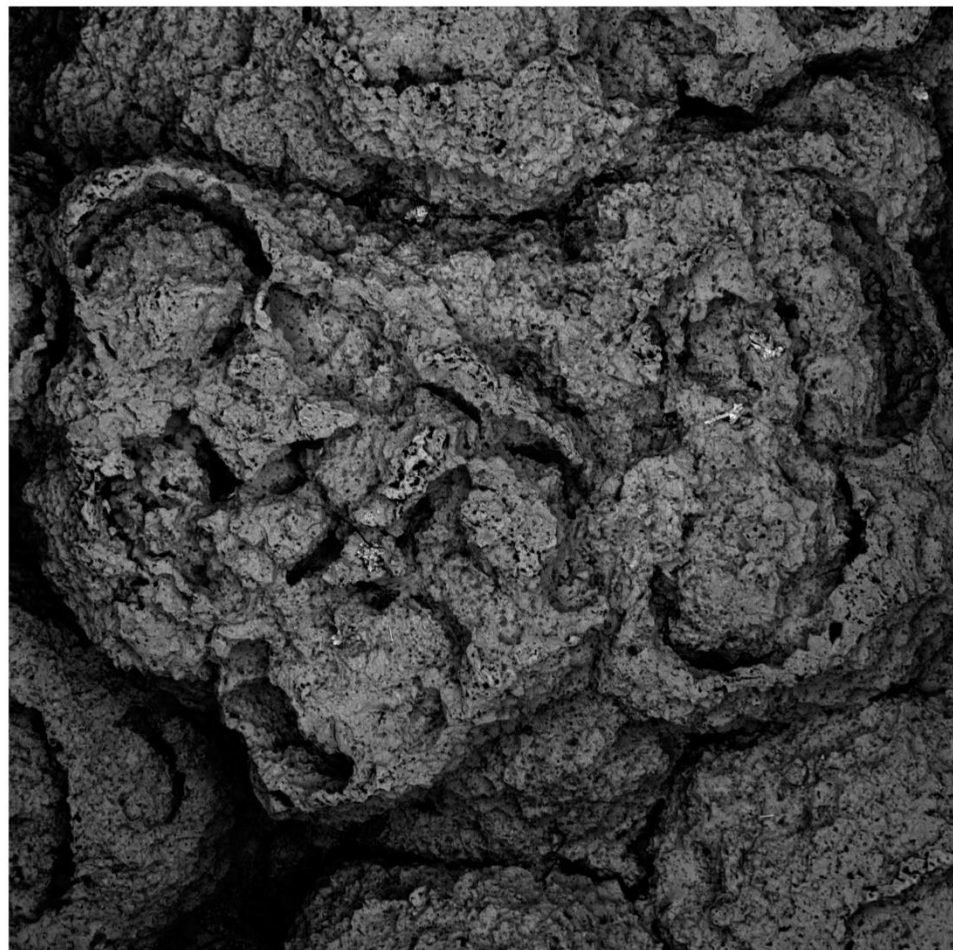


Wikipedie



Pec pod Sněžkou, Kutná Hora (Kaňk), Roudný, Mokrsko, Příbram, Jáchymov, Jílové a mnoho dalších lokalit...

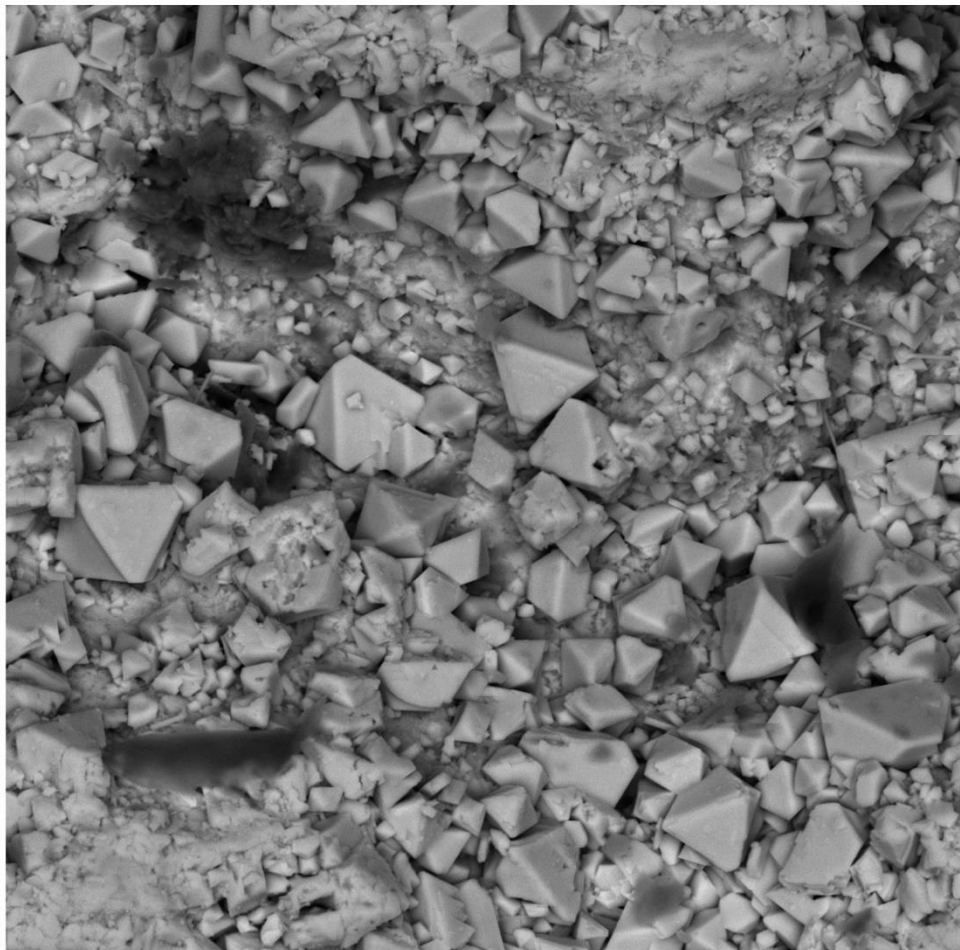
Vzorek k prohlídce: ryzí arzén



neplacaty_2
SEM HV: 20.0 kV
HiVac
WD: 14.87 mm
Det: BSE
SEM MAG: 80 x

2 mm

VEGA3 TESCAN
GLU AVCR



neplacaty_1
SEM HV: 20.0 kV
HiVac
WD: 23.19 mm
Det: BSE
SEM MAG: 3.84 kx

20 µm

VEGA3 TESCAN
GLU AVCR

Výskyt arzén v životním prostředí

PŘIROZENÝ VÝSKYT

- Rudní minerály arzénu: **arzenopyrit**, stibarsen (allemontit), ryzí arzén, sekundární minerály (realgar)
- Rudní minerály s arzénem: pyrit, markazit, galenit, sfalerit
- Uhlí (12-18¹, 40², 333³ mg/kg).
- Sopečná činnost (plyny)

ANTROPOGENNÍ ZDROJE

- Těžba a zpracování rud
- Energetika (tepelné elektrárny)
- Zemědělství (pesticidy, CCA⁴)



¹ průměrný obsah v uhlí, ² průměr ze Severočeské pánve, ³ průměr ze Sokolovské pánve

⁴ chromated copper arsenate (chemické ošetření dřeva)

Arzén v životním prostředí

Distribuce a speciace prvků v biosféře je důsledkem procesů, jichž se zúčastňují živé organismy včetně člověka. Normální koncentrace **arzénu** ve složkách ŽP:

Zemská kůra: 1,8-2,5 mg/kg

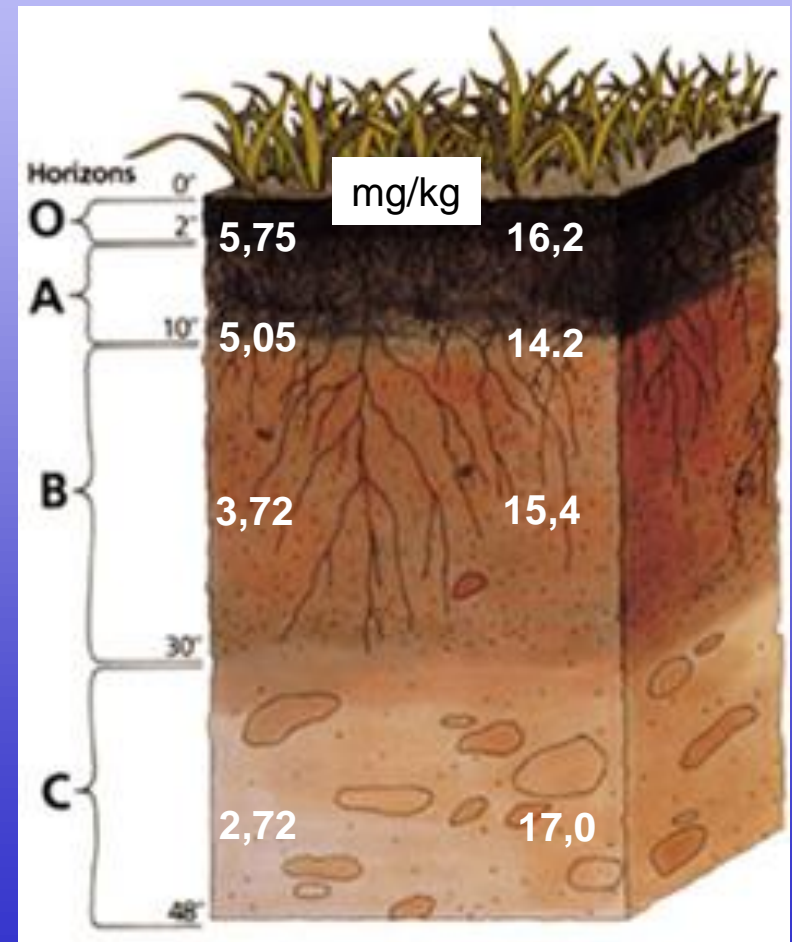
Žula: 1,5-2,5 mg/kg

Bazalt (čedič): 0,5-2,5 mg/kg

Vápenec: 1-2,5 mg/kg

Pískovec: 0,5-1,2 mg/kg

Půdy: 1-30 mg/kg

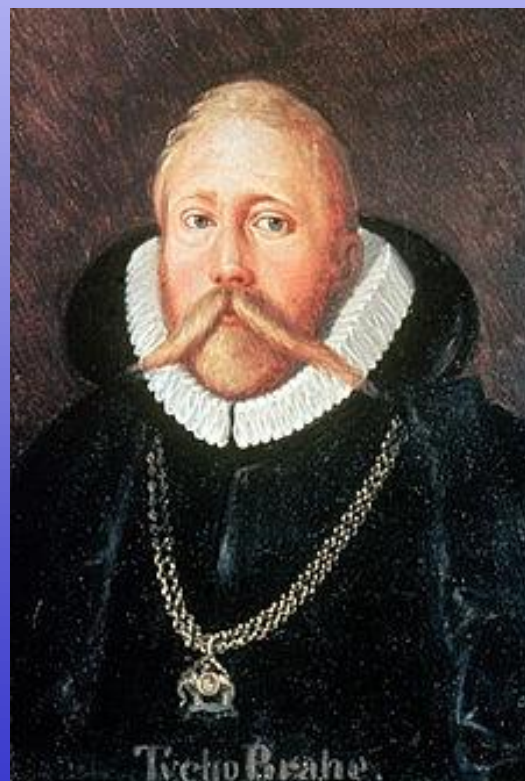


PRINCIP VŠUDYPŘÍTOMNOSTI PRVKŮ

Chemické prvky jsou všudypřítomné (kromě nestabilních radioaktivních izotopů), vše je otázkou koncentrace.

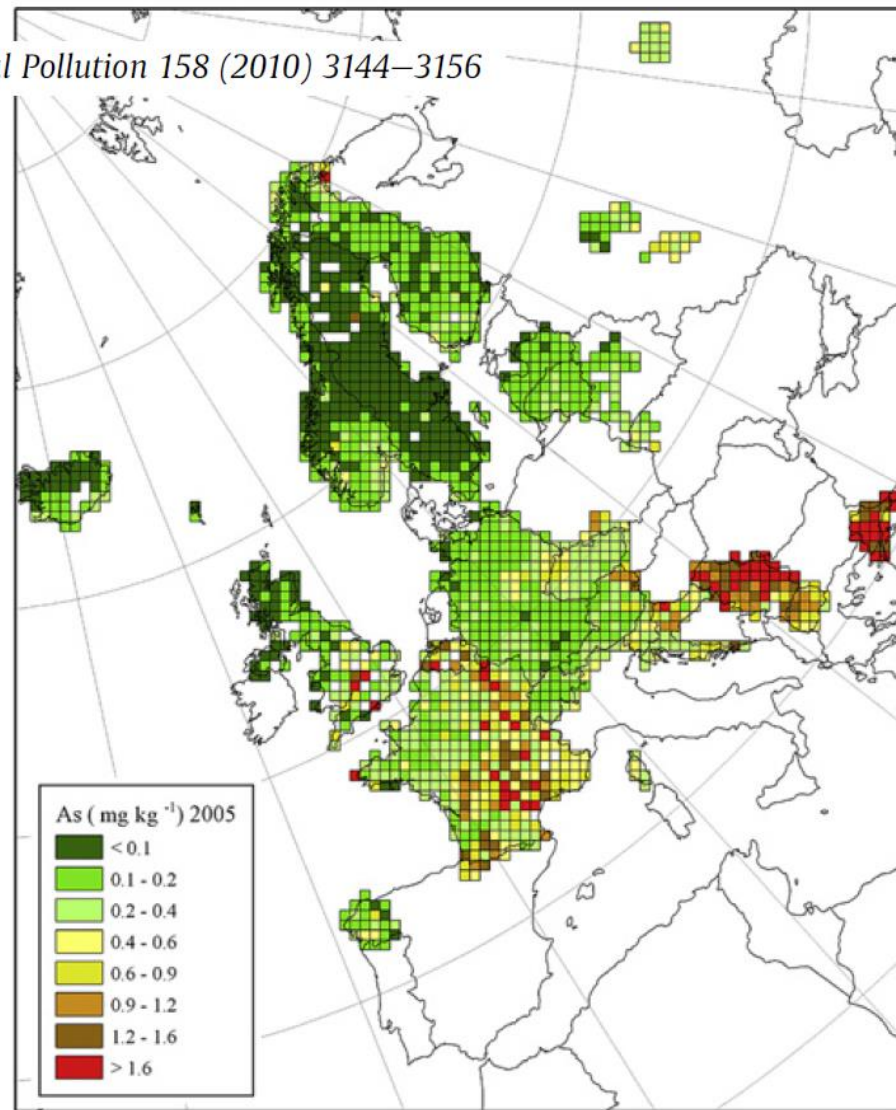
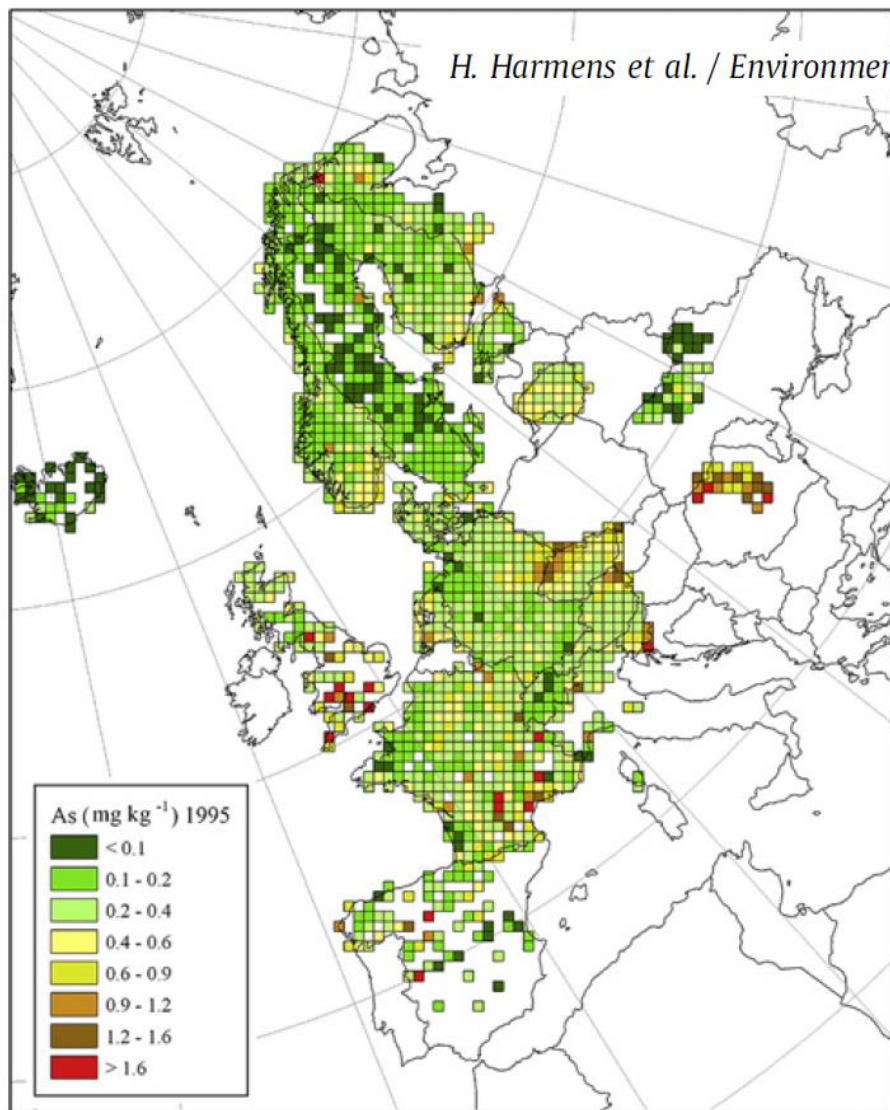
Základním předpokladem pro takové studium chemických prvků jsou rozvinuté metody analytické chemie: tj. možnost stanovit koncentrace arzenu.

AAS, ICPOES, ICPMS, INAA



Geochemický monitoring: koncentrace As v meších v letech 1995 a 2005



H. Harmens et al. / Environmental Pollution 158 (2010) 3144–3156

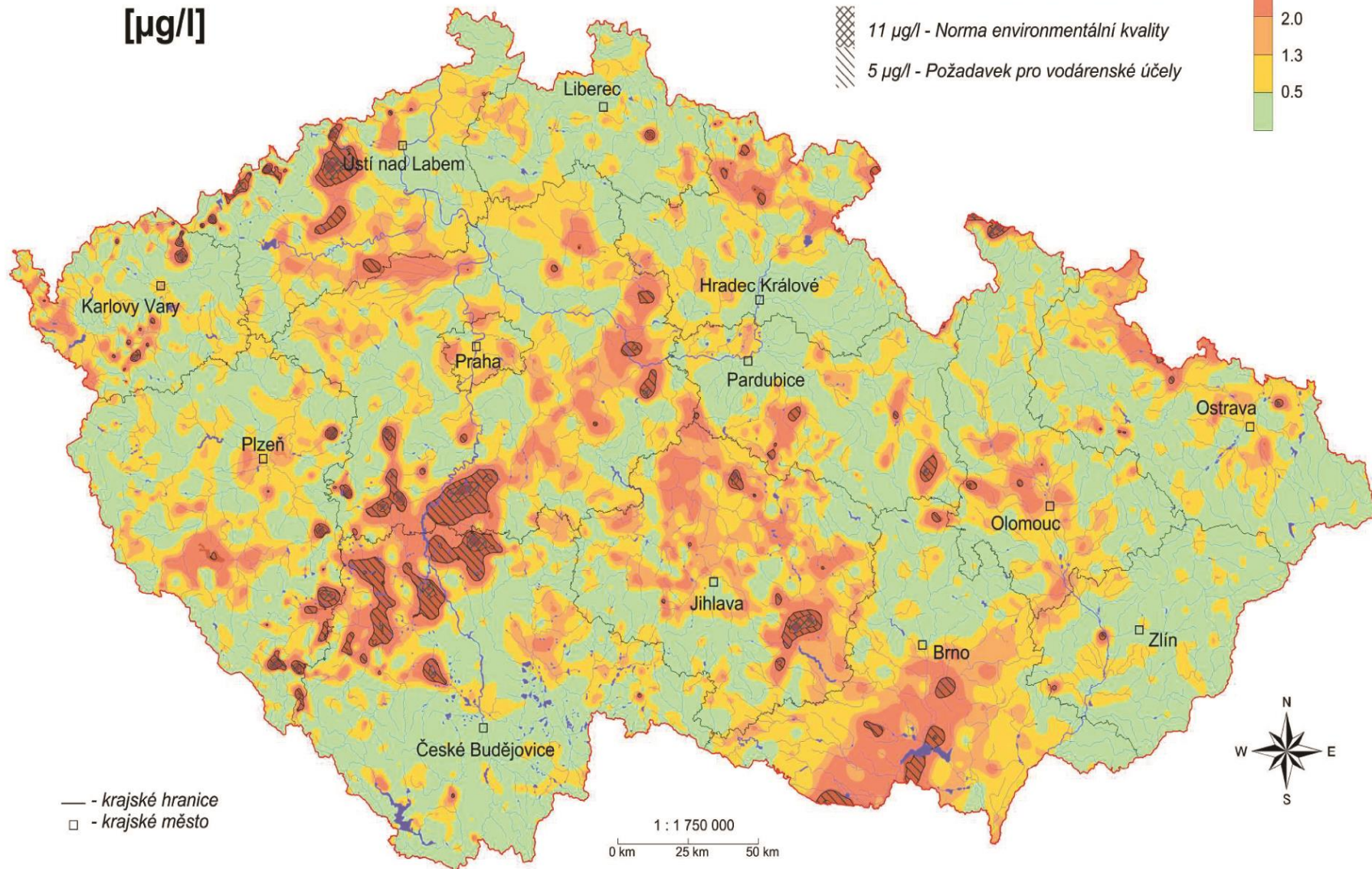
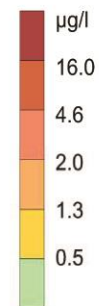


Obsah arsenu v povrchových vodách České republiky v letech 2007-2010

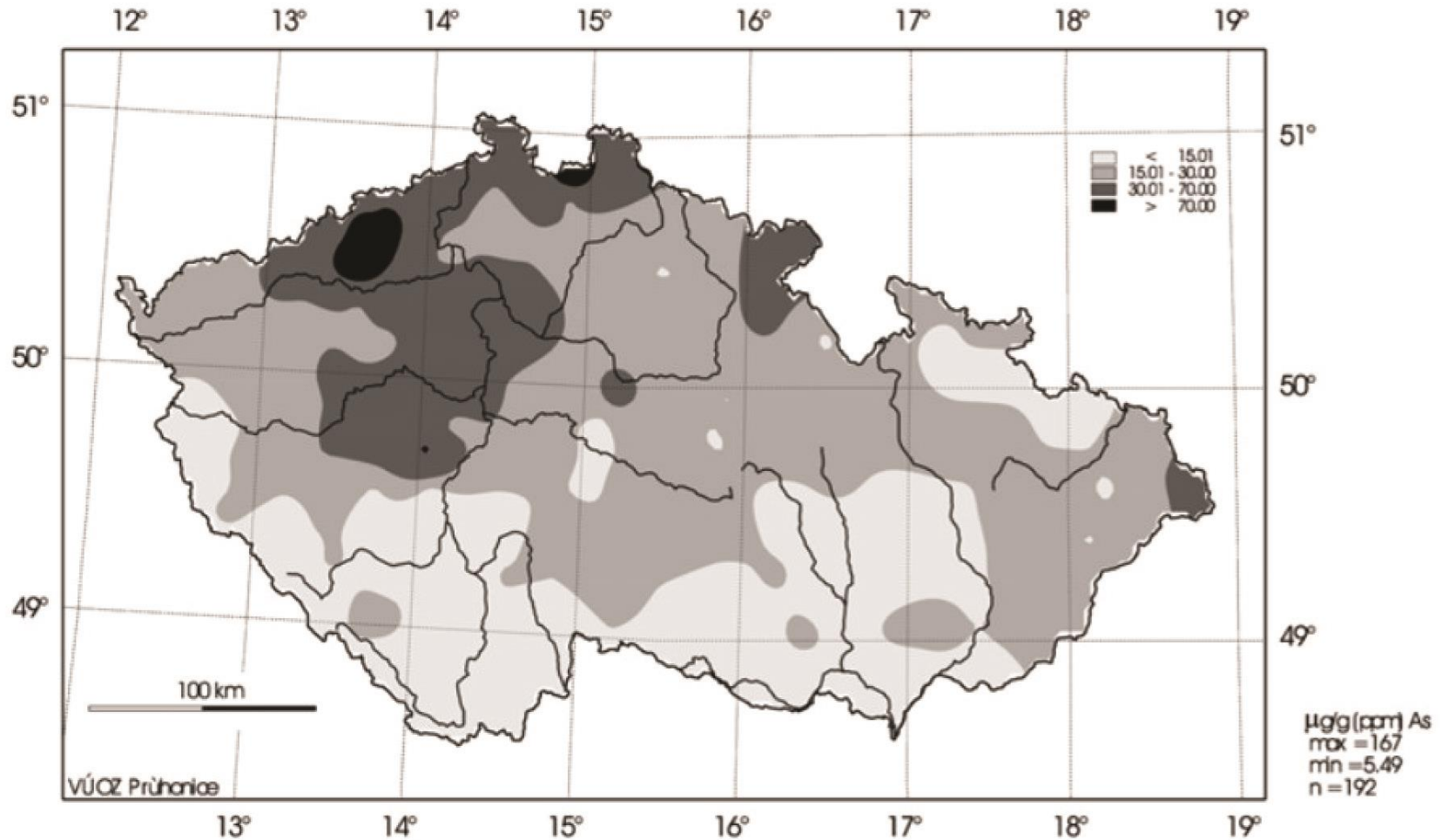
As
[$\mu\text{g/l}$]

**Překročení přípustného znečištění
(61/2003 Sb. ve znění novely 23/2011 Sb.)**

 11 $\mu\text{g/l}$ - Norma environmentální kvality
 5 $\mu\text{g/l}$ - Požadavek pro vodárenské účely



Arzén v humusu jehličnatých lesů v ČR v roce 1995



Arsenic Content of Food and Forage Plants from Various Countries^a (µg/kg)

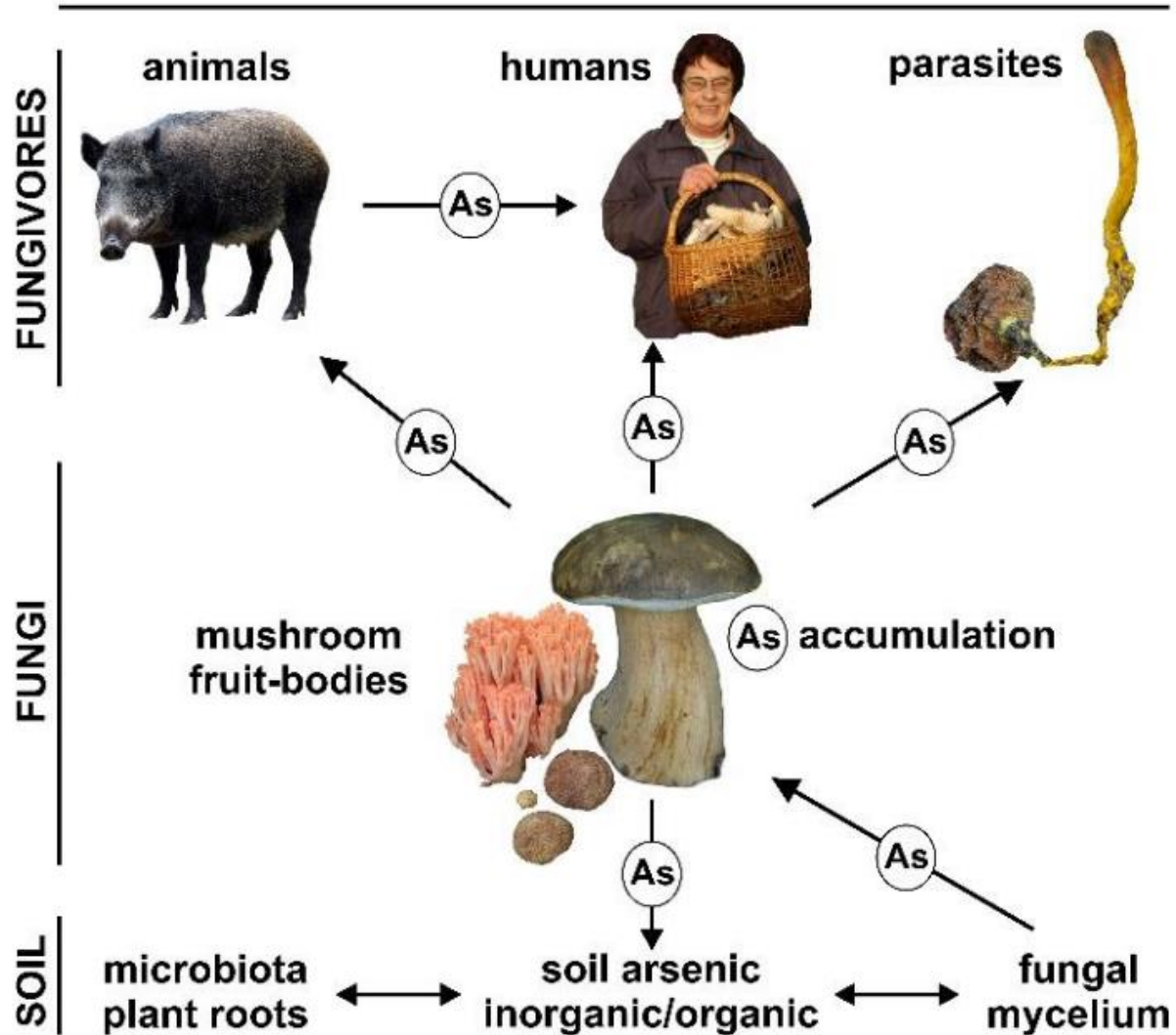
Plant	Sample	Range/Mean
Barley	Grains	3–18
Oats	Grains	10
Wheat	Grains	3–10
Rice	Grains	0.5–10
Corn/maize ^b	Grains	1848
Snap beans	Pods	1.3–7
Cabbage	Leaves	20–69
Lettuce	Leaves	20–50
Carrot	Roots	10–80
Potato	Tubers	10–20
Potato ^b	Tubers	864
Tomato	Fruits	9–12
Orange	Fruits	11–50
Edible mushroom	Whole	280
Clover	Tops	20–160
Grass	Tops	280–330 1000–5400 ^c

^a Presented are common, possible background values from various sources, unless otherwise indicated.

^b Plants from Chile, after Queirolo et al. (2000).

^c Grass from climatic zone (Kazakhstan).¹¹³¹

Arzén v mykosféře



Arzén v houbách

Půdy: 1-30 mg/kg As, průměrně 7 mg/kg.

Houby: akumulují As, a to hlavně saprotrofové. Data z dostupné literatury (2005) pro čisté lokality (mg/kg sušiny):

	SAP	ECM	SAP _{lig}
medián	1.60	0.53	0.54
aritmetický průměr	4.16	1.14	1.01
geometrický průměr	1.84	0.48	0.47
maximum	52.4	23.4	11.8
minimum	0.13	0.02	0.02
n	174	247	48

Arzén v houbách

V Evropě rostou tisíce druhů velkých hub, koncentrace As ve většině z nich nejsou známy.

V období let 2003-2018 jsme shromáždili asi 2000 vzorků (nikoliv druhů) hub, z nichž většina byla analyzována.

Byly odhaleny významné akumulace As až do hodnot přesahujících 10 000 mg/kg na čistých lokalitách.

V letech 2016-2018 probíhal výzkum (tříletý mezinárodní projekt ve spolupráci s Univerzitou ve Štýrském Hradci) zaměřený na **chemické složení arzenu v houbách.**

Arzén v houbách: faktory

Druhová závislost koncentrace.

Zvýšené koncentrace As v prostředí vedou ke zvýšeným koncentracím As v houbách.

Oblasti s přirozenou a antropogenní kontaminací.

Mokrsko

- ložisko zlata s vysokým výskytem arzenopyritu
- As v půdách často vyšší než 1000 mg/kg
- běžné houby mají As v průměru 10x zvýšený



**STOP
TĚŽBĚ ZLATA**



Arzénové sloučeniny v houbách: záhada původu

V půdním roztoku jsou dominantní **anorganické sloučeniny arzénu**

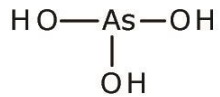
- arseničnanové (V) ionty AsO_4^{3-}
- arsenitanové (III) ionty AsO_3^{3-}

V houbách obvykle dominují **organické, metylované formy** arzénu (tj. s jednou či více vázaných $-\text{CH}_3$ skupin).

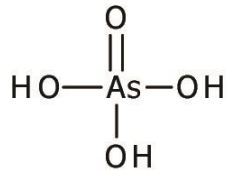
Metylace arzénu byla prokázána u bakterií a některých mikroskopických hub. Mycelia velkých hub pěstovaná *in vitro*, exponovaná arzénu [As(III) I As(V)], však ani při dlouhodobé expozici v drtivé většině testovaných případů nevykazují přítomnost metylovaných sloučenin arzénu.

Hlavní formy arzénu v plodnicích hub

anorganické

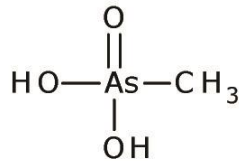


As (III)

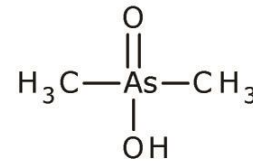


As (V)

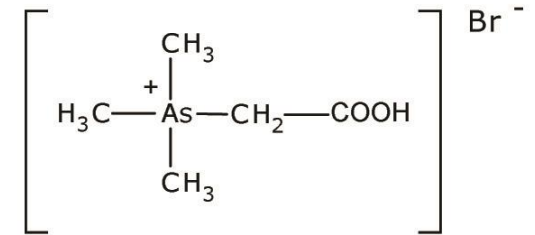
organické



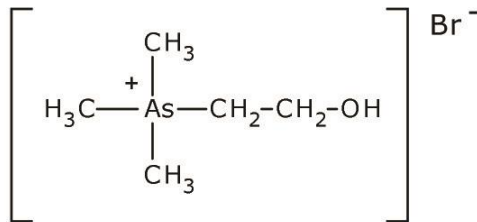
methyларsonová kys.



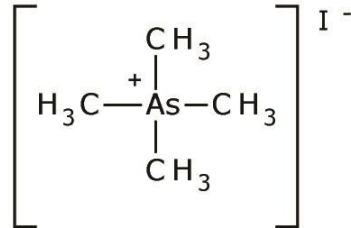
dimethylarsinová kys.



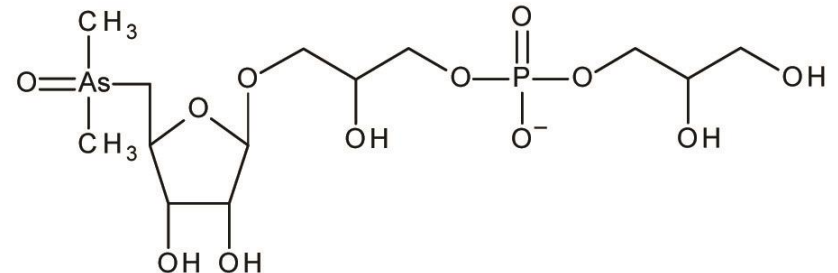
arsenobetain



arsenocholin



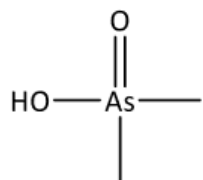
tetramethylarsoniový iont



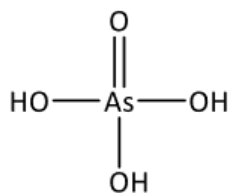
arsenosacharid

Běžné a vzácné formy arzénu v houbách

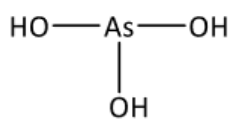
Main species



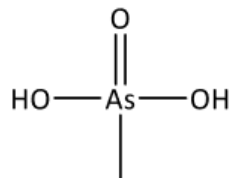
Dimethylarsinic acid
[DMA]



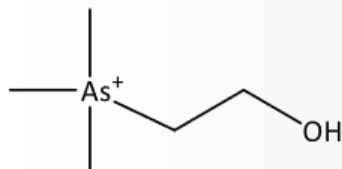
Arsenic acid
[As(V)]



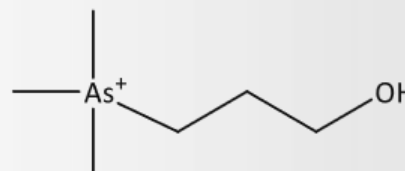
Arsenous acid
[As(III)]



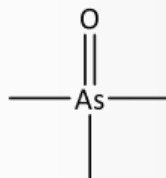
Methylarsonic acid
[MA]



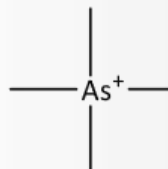
Arsenocholine
[AC]



Homoarsenocholine
[AC2]

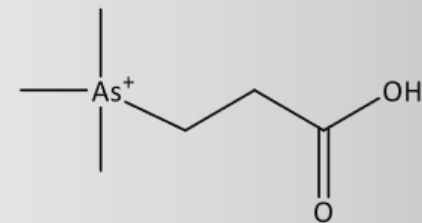


Trimethylarsine oxide
[TMAO]

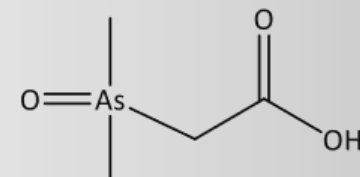


Tetramethylarsonium ion
[TETRA]

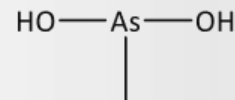
Less common species



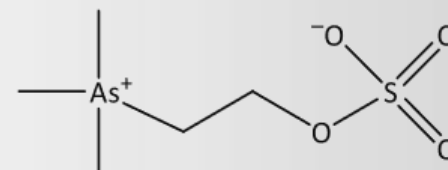
Trimethylarsoniopropionic acid
[TMAP, AB2]



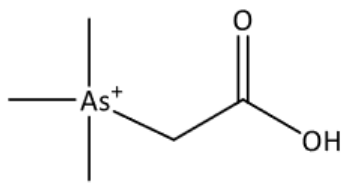
Dimethylarsinoylacetic acid
[DMAA]



Methylarsonous acid
[MA(III)]



Arsenocholine-O-sulfate
[AC-SO₄]



Arsenobetaine
[AB]

Konkurenční tým v Kanadě:

Environmental Pollution 197 (2015) 108–115



Contents lists available at [ScienceDirect](#)

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol



Uptake and transformation of arsenic during the vegetative life stage of terrestrial fungi



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ARTICLE INFO

Article history:

Received 21 September 2014

Received in revised form

25 November 2014

Accepted 1 December 2014

Available online 15 December 2014

Keywords:

Arsenobetaine

Arsenic

Mycelium

Biotransformation

Concentration factor

ABSTRACT

Many species of terrestrial fungi produce fruiting bodies that contain high proportions of arsenobetaine (AB), an arsenic compound of no known toxicity. It is unknown whether fungi produce or accumulate AB from the surrounding environment. The present study targets the vegetative life stage (mycelium) of fungi, to examine the role of this stage in arsenic transformations and potential formation of AB. The mycelia of three different fungi species were cultured axenically and exposed to AB, arsenate (As(V)) and dimethylarsinoyl acetic acid for 60 days. *Agaricus bisporus* was additionally exposed to hypothesized precursors for AB and the exposure time to As(V) and dimethylarsinic acid was also extended to 120 days. The mycelia of all fungi species accumulated all arsenic compounds with two species accumulating significantly more AB than other compounds. Few biotransformations were observed in these experiments indicating that it is unlikely that the mycelium of the fungus is responsible for biosynthesizing AB.

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Table 2
Average arsenic species concentration, column recovery (CR) and extraction efficiency (EE) of mycelium.

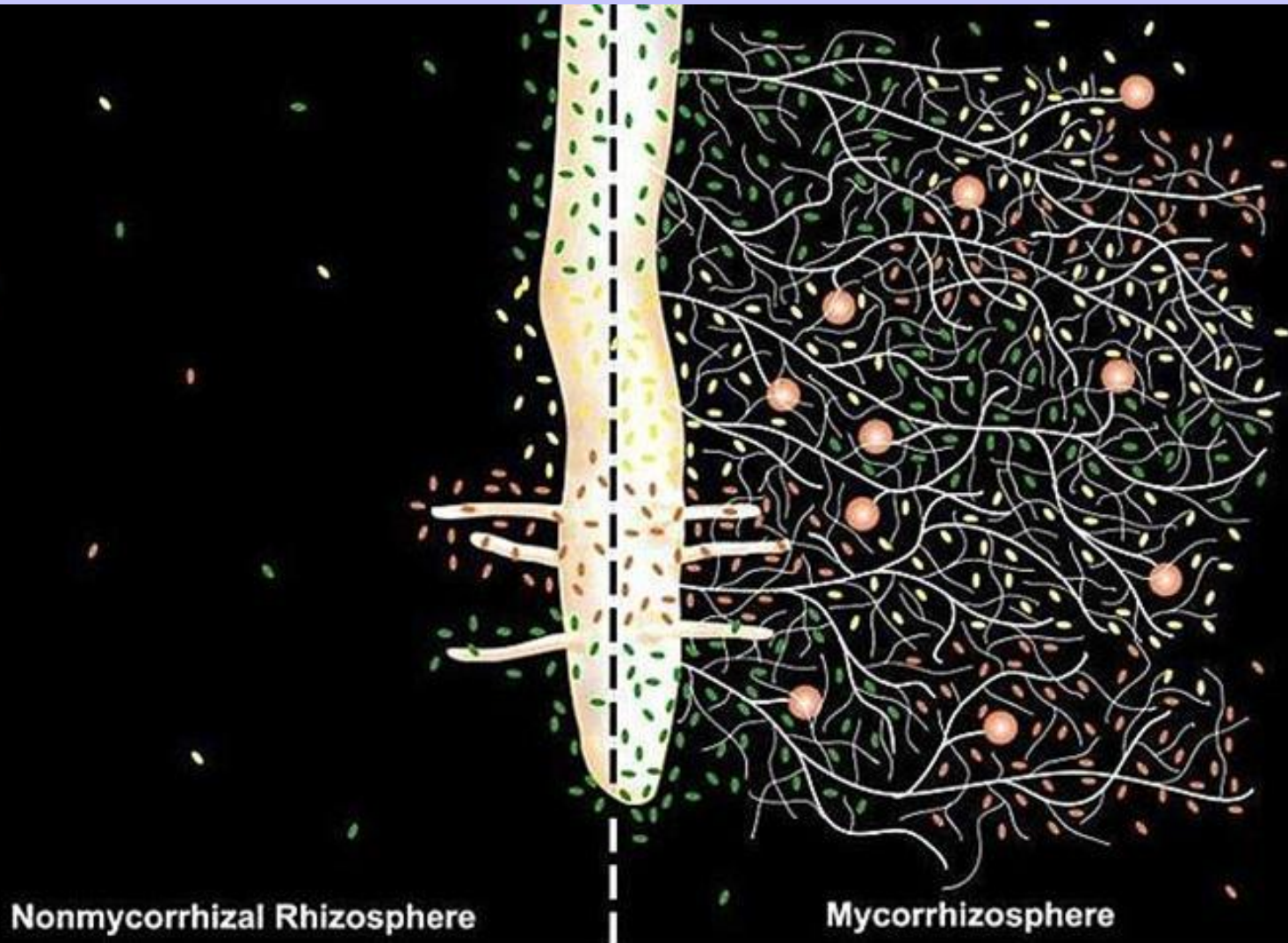
Fungus species	Treatment	As compounds (ug/kg wet weight)							Column recovery (%)	Extraction efficiency (%)
		As III	As V	MMA	DMA	TMAO	DMAA	AB		
<i>A. bisporus</i>	Control ^A	130 ± 9	nd	nd	nd	nd	nd	nd	140 ± 30	80 ± 20
	As(V) ^A	trace	70 ± 40	nd	nd	nd	nd	nd	120 ± 10	34 ± 10
	DMAA ^A	trace	nd	nd	nd	nd	190 ± 40	nd	110 ± 10	85 ± 8
	AB ^A	51 ± 60	nd	nd	nd	nd	nd	240 ± 40	90 ± 20	96 ± 2
	Control ^B	nd	nd	nd	nd	nd	nd	nd	NC	NC
	As(V) 60 days ^B	104.8 ± 0.8	80 ± 5	nd	nd	nd	nd	nd	110 ± 10	74 ± 20
	As(V) 90 days ^B	210 ± 20	150 ± 100	nd	nd	nd	nd	nd	80 ± 30	85 ± 11
	As(V) 120 days ^B	280 ± 100	150 ± 200	trace	trace	nd	nd	nd	90 ± 70	90 ± 3
	DMA 60 days ^B	nd	nd	nd	300 ± 9	nd	nd	nd	110 ± 4	73 ± 20
	DMA 90 days ^B	nd	nd	nd	500 ± 4	nd	nd	nd	100 ± 2	90 ± 4
	DMA 120 days ^B	nd	nd	nd	800 ± 20	nd	nd	nd	100 ± 20	68 ± 4
	Control ^C	nd	nd	nd	nd	nd	nd	nd	NC	NC
	MMA ^C	nd	nd	150 ± 10	nd	nd	nd	nd	110 ± 10	NC
	TMAO ^C	nd	nd	nd	nd	160 ± 100	nd	nd	92 ± 30	NC
DMA 30 days ^C	nd	nd	nd	140 ± 40	nd	nd	nd	80 ± 10	NC	
<i>S. luteus</i>	Control	trace	trace	nd	nd	nd	nd	nd	NC	82 ± 2
	As(V)	110 ± 40	trace	nd	nd	nd	nd	nd	83 ± 20	70 ± 10
	DMAA	trace	222*	nd	nd	nd	180 ± 80	nd	110 ± 20	90 ± 10
	AB	trace	nd	nd	nd	nd	nd	70 ± 30	100 ± 20	87 ± 10
<i>S. crispa</i>	Control	trace	60 ± 70	nd	nd	nd	nd	nd	140 ± 100	98 ± 3
	As(V)	trace	270 ± 10	nd	nd	31 ± 3	nd	nd	100 ± 7	93 ± 3
	DMAA	trace	165*	nd	nd	nd	110 ± 70	nd	110 ± 30	96 ± 1
	AB	nd	nd	nd	nd	nd	nd	580 ± 60	100 ± 7	97 ± 1

^{A B C} Control mycelium (no As) corresponds to treatments with the same letter.

* indicates only observed in one replicate, nd = non-detect (<3 µg/kg), trace <5 µg/kg, NC = not calculated.

Column recovery = (Sum of arsenic compounds/Total As in extract)*100, Extraction Efficiency = (Total As in extract/Total As in mycelium)*100.

Pocházejí organosloučeniny As z půdy?



Akutní **toxicita** sloučenin arzénu

LD₅₀ je v toxikologii označení pro dávku látky podané testovaným jedincům, která způsobí úhyn 50 % testovaných živočichů do 24 hodin od expozice. Udává se v mg/kg živé hmotnosti.

Sloučenina arsenu	Zkratka	LD ₅₀ (mg/kg)
Arsenitan	As ^{III}	15 – 42
Arseničnan	As ^V	20 – 800
Monometylarsonát	MMA	700 – 1800
Dimetylarzinát	DMA	1200 – 2600
Trimetylarzin oxid	TMAO	10600
Tetrametylarsoniový ion	TETRA	890
Arsenocholin	AC	6500
Arsenobetain	AB	> 10000

toxický

netoxický

Stanovení sloučenin As v houbách

Sloučeniny As v houbách jsou poměrně stabilní (na rozdíl od sloučenin Sb), lze je efektivně extrahovat.

Extrakce: namletý vzorek (100 mg) sušené či lyofilizované houby se extrahuje ve vodě nebo v metanolu.

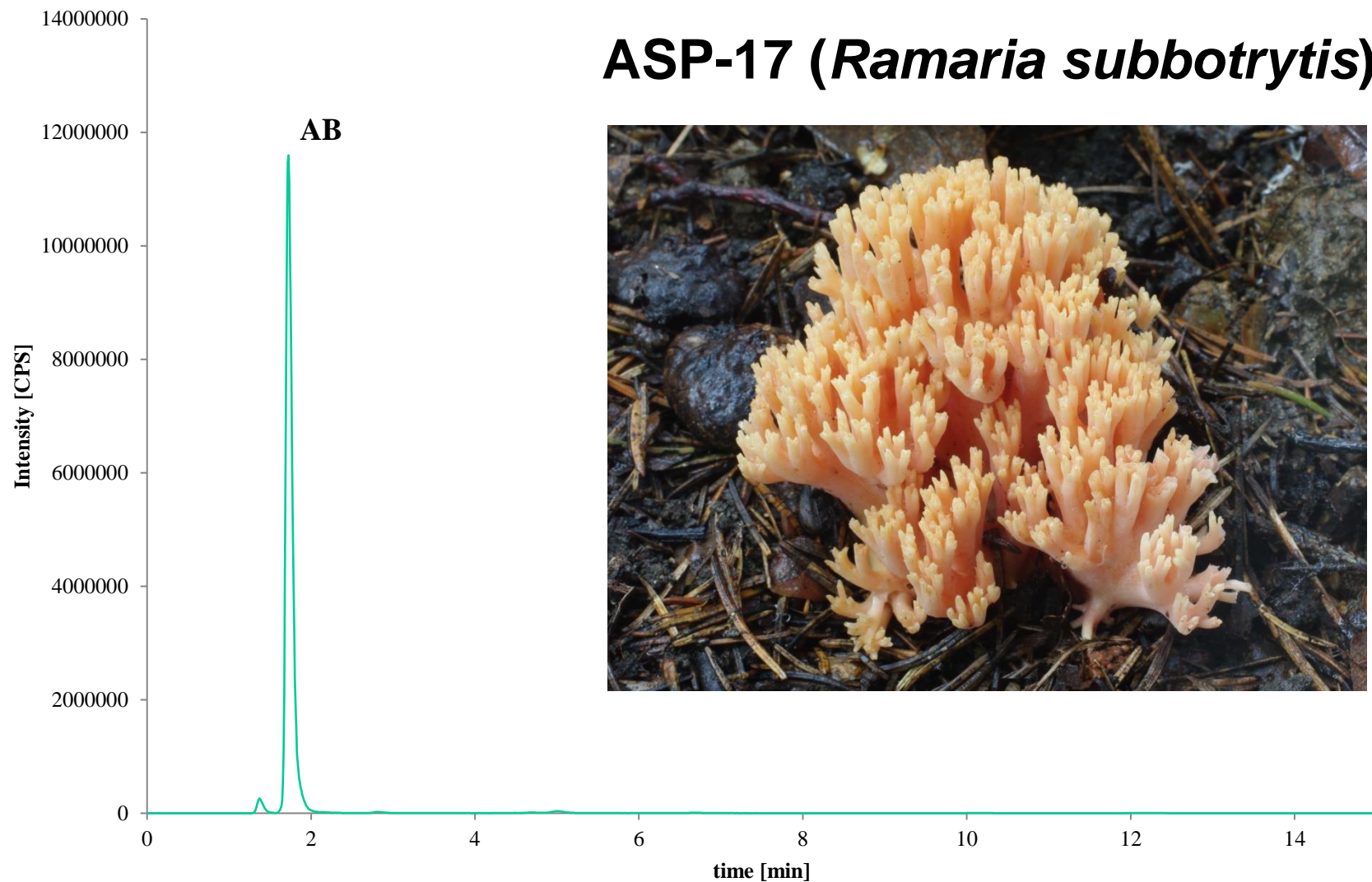
HPLC-ICPQQMS

vysokotlaká kapalinová chromatografie kombinovaná s ICPQQMS

Přítomnost látek s As + jejich identifikace.



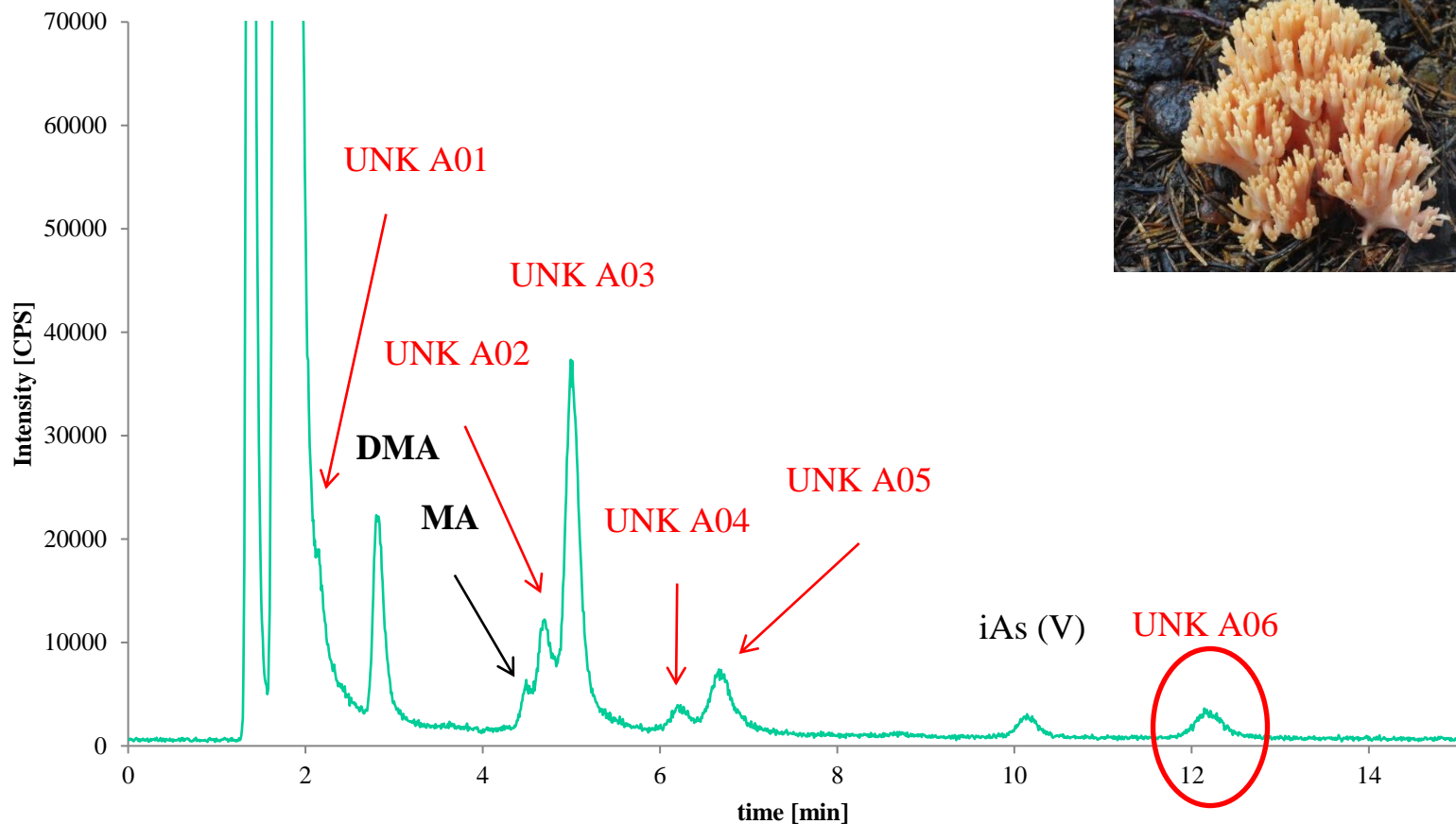
Stanovení sloučenin As v houbách

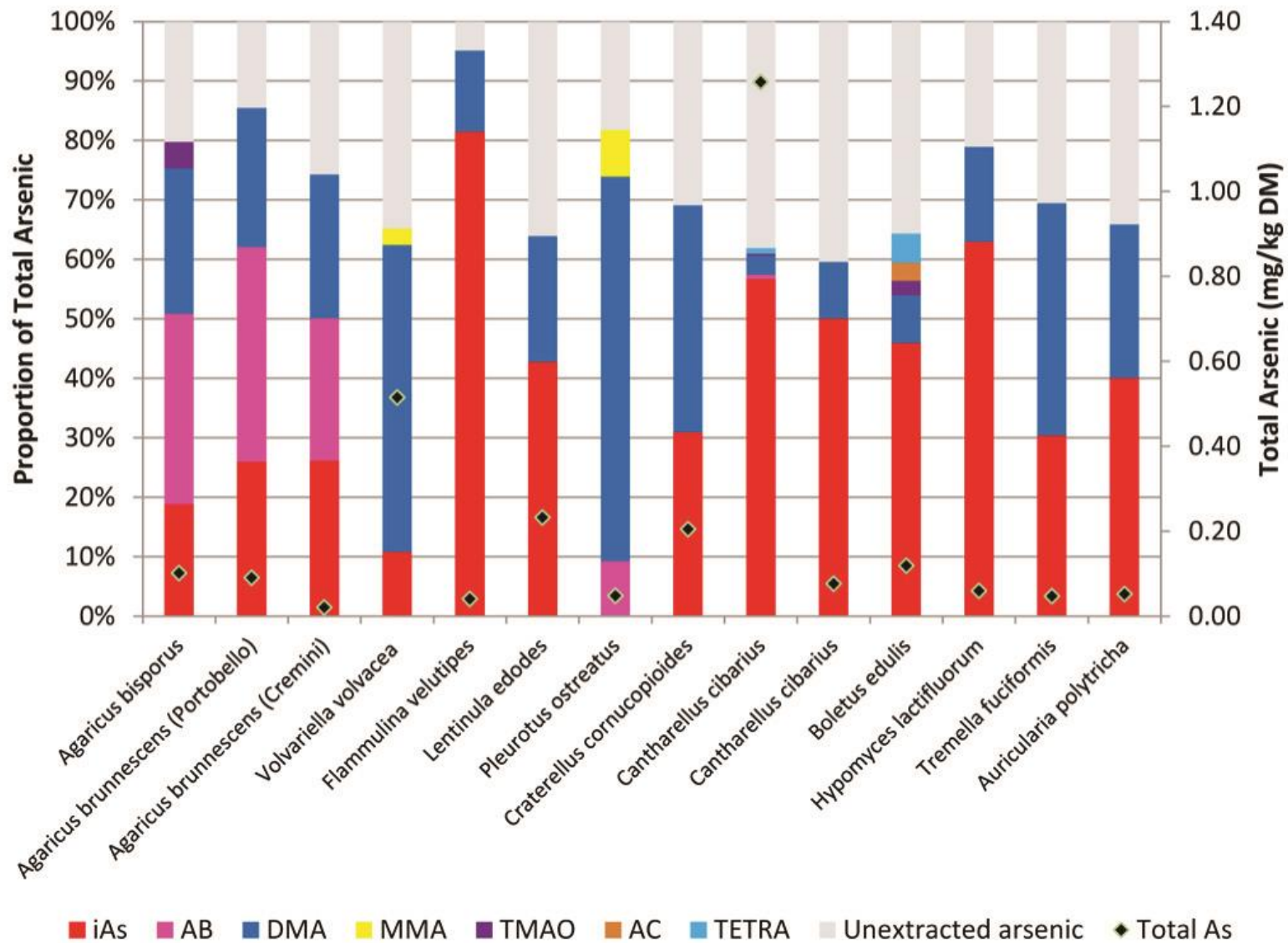


Stanovení sloučenin As v houbách

ASP-17 (*Ramaria subbotrytis*) - zoom

AB





Průměrné zastoupení sloučenin As (levá osa), celkového arzénu (pravá osa + body) v tržních houbách z Kanady.



Pečárka lesní – *Agaricus sylvaticus*

Baňka veľkokališná – *Sarcosphaera coronaria*





Lakovka ametystová – *Laccaria amethystina*

Plesňák zemní – *Thelephora terrestris*



Vláknice tuřínonohá – *Inocybe napipes*



Čirůvka větší – *Tricholoma matsutake*



Pavučinaec sivonohý – *Cortinarius glaucopus*



Pavučinaec proměnlivý – *Cortinarius polymorphus*



Olšovka zlatá – *Alnicola xanthophylla*



Pavučinec olšinný – *Cortinarius alnetorum*



ANALYTICAL & BIOANALYTICAL CHEMISTRY



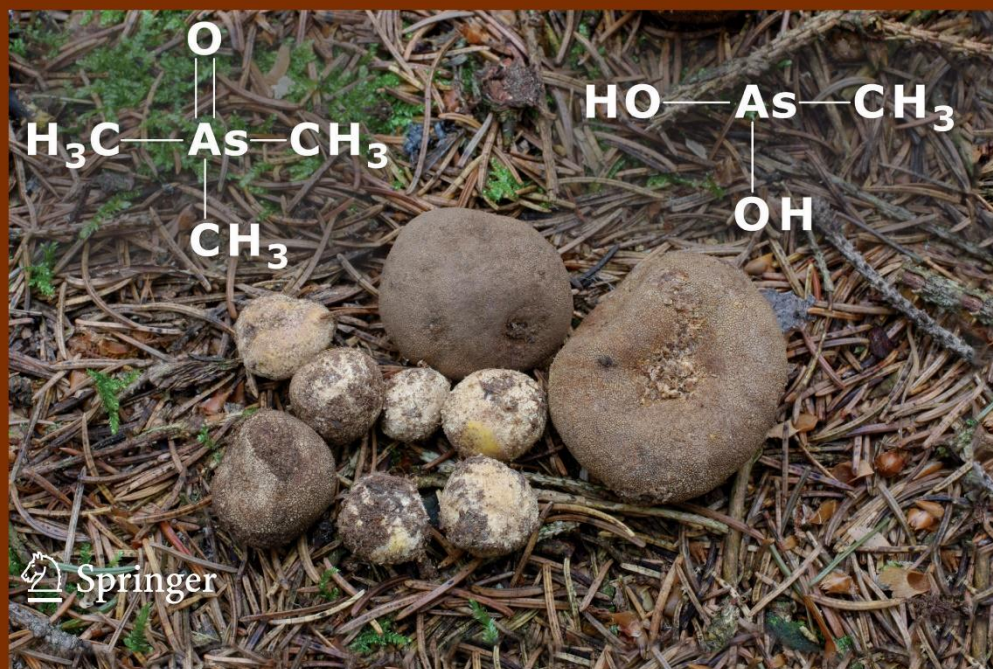
ASAC



216

ANALYTICAL & BIOANALYTICAL CHEMISTRY Vol 410 · No 9 · March 2018 · pp xxx-xxxx

ABC presents bioanalysis and environmental analysis
 Flipped learning for delivery of analytical chemistry topics
 Analytical challenges in sports drug testing
 Unique arsenic speciation profile in *Elaphomyces* spp.



Jelenka pestrá – *Elaphomyces muricatus*



Jelenka obecná – *Elaphomyces granulatus*



Moje pracoviště...





A unique arsenic speciation profile in *Elaphomyces* spp. (“deer truffles”) —trimethylarsine oxide and methylarsonous acid as significant arsenic compounds

Simone Braeuer¹ · Jan Borovička^{2,3} · Walter Goessler¹

TMAO, MA, MA (III)*
***vysoce toxická**

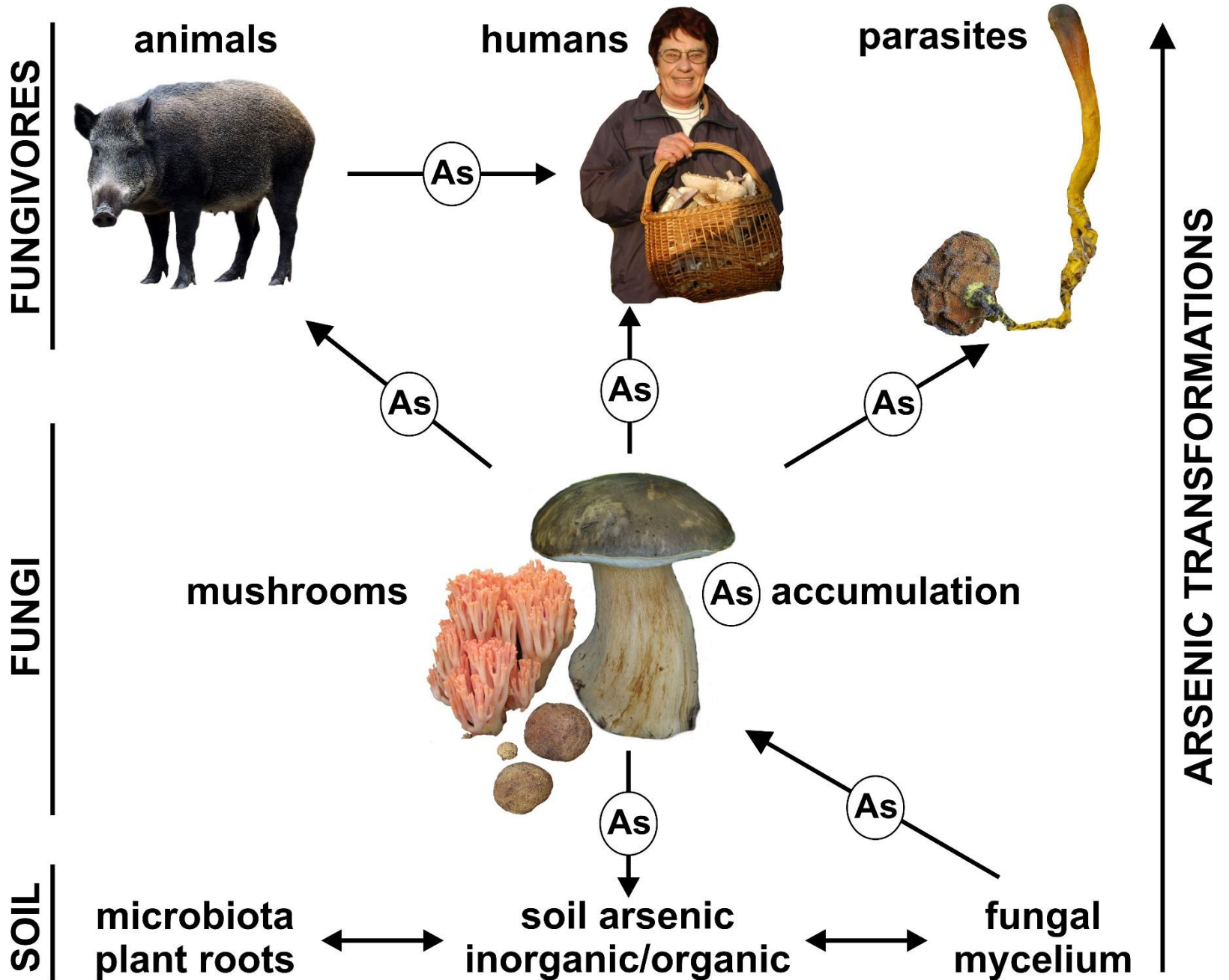
Received: 31 October 2017 / Revised: 21 December 2017 / Accepted: 18 January 2018
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Abstract

Arsenic and its species were investigated for the first time in nine collections of *Elaphomyces* spp. (“deer truffles”) from the Czech Republic with inductively coupled plasma mass spectrometry (ICPMS) and high-performance liquid chromatography coupled to ICPMS. The total arsenic concentrations ranged from 12 to 42 mg kg⁻¹ dry mass in samples of *E. asperulus* and from 120 to 660 mg kg⁻¹ dry mass in *E. granulatus* and *E. muricatus*. These concentrations are remarkably high for terrestrial organisms and demonstrate the arsenic-accumulating ability of these fungi. The dominating arsenic species in all samples was methylarsonic acid which accounted for more than 30% of the extractable arsenic. Arsenobetaine, dimethylarsinic acid, and inorganic arsenic were present as well, but only at trace concentrations. Surprisingly, we found high amounts of trimethylarsine oxide in all samples (0.32–28% of the extractable arsenic). Even more remarkable was that all but two samples contained significant amounts of the highly toxic trivalent arsenic compound methylarsonous acid (0.08–0.73% of the extractable arsenic). This is the first report of the occurrence of trimethylarsine oxide and methylarsonous acid at significant concentrations in a terrestrial organism. Our findings point out that there is still a lot to be understood about the biotransformation pathways of arsenic in the terrestrial environment.

Keywords *Elaphomyces* · Fungi · Deer truffles · Arsenic speciation · Trimethylarsine oxide · Methylarsonous acid

MYCOSPHERE





Elaphomyces granulatus, Aim 2



Tolypocladium ophioglossoides, Aim 2



E. muricatus with *T. ophioglossoides* mycelial cords, Aim 2

Arsenocholine-*O*-sulfate: A novel compound as major arsenic species in the parasitic mushroom *Tolypocladium ophioglossoides*



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HIGHLIGHTS

- Arsenocholine-*O*-sulfate was discovered for the first time in nature.
- Arsenocholine-*O*-sulfate was the main As species in *Tolypocladium ophioglossoides*.
- Concentrations of As species and 35 elements were determined in *T. ophioglossoides*.
- Hosts, *Elaphomyces* spp., show different elemental profiles than *T. ophioglossoides*.

ARTICLE INFO

Article history:

Received 16 September 2020

Received in revised form

26 October 2020

Accepted 4 November 2020

Available online 7 November 2020

Handling Editor: Lena Q. Ma

Keywords:

Arsenic speciation analysis

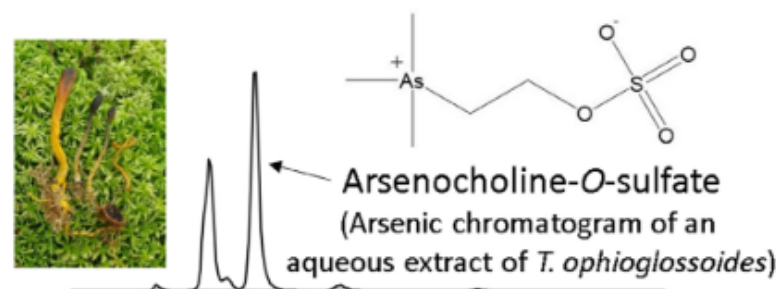
Fungi

Arsenic transformation

Arsenocholine

ICPMS

GRAPHICAL ABSTRACT

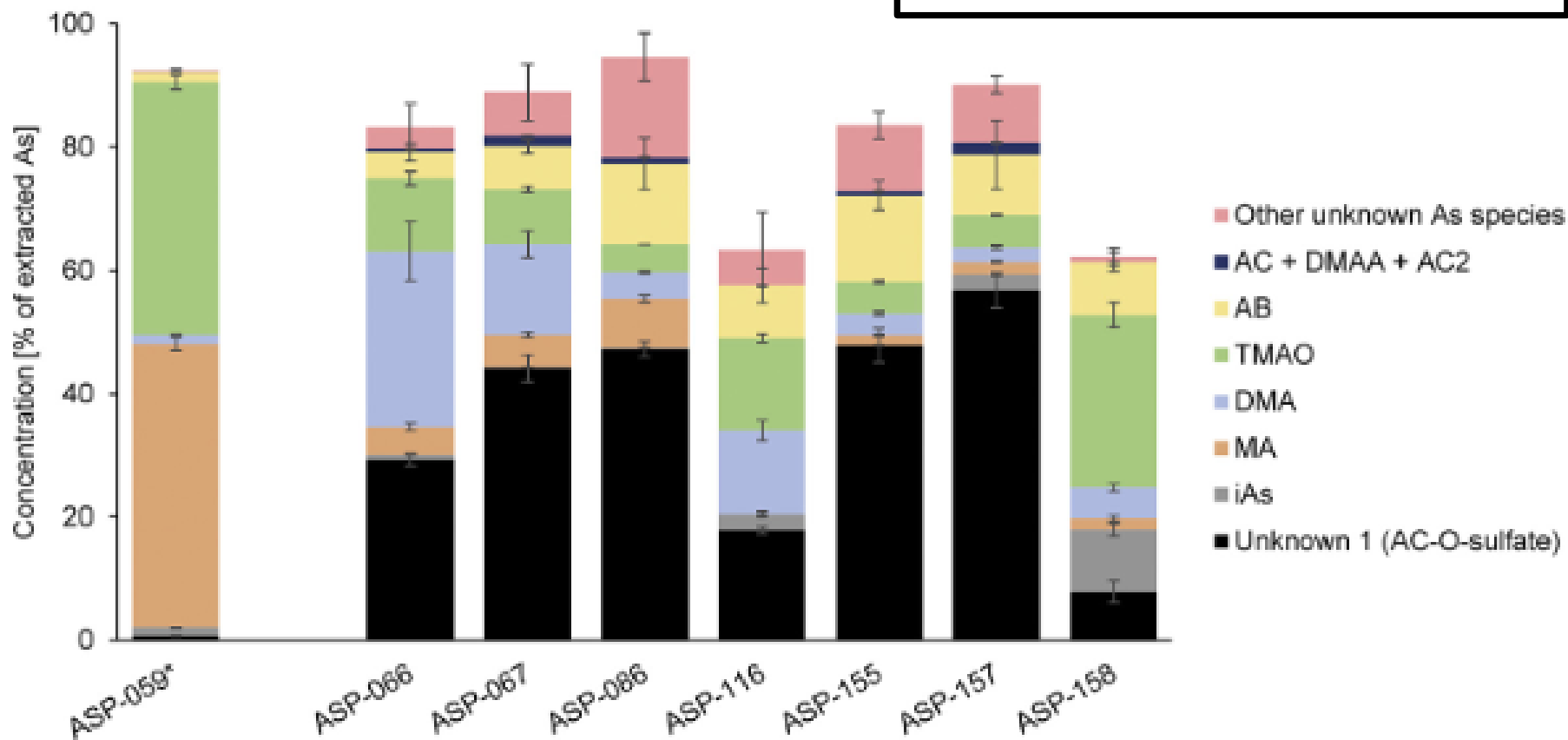
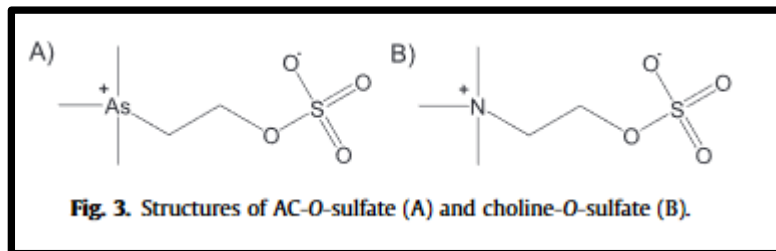


ABSTRACT

The As concentrations, along with 34 other elements, and the As speciation were investigated in wild-grown samples of the parasitic mushroom *Tolypocladium ophioglossoides* with inductively coupled plasma mass spectrometry (ICPMS) and high performance liquid chromatography coupled to ICPMS. The As concentrations were 0.070–3.44 mg kg⁻¹ dry mass. More remarkable was the As speciation, where up to 56% of the extracted As were found to be an unknown As species, which was marginally retained under anion- and also cation-exchange conditions. After testing several different chromatographic settings, the compound was finally isolated and identified as 2-(sulfoxyethyl) trimethylarsonium ion (in short: arsenocholine-*O*-sulfate) with high resolution mass spectrometry. The compound was synthesized and further quantified in all investigated samples via ion-pair chromatography coupled to ICPMS. In addition to the high abundance of arsenocholine-*O*-sulfate in *T. ophioglossoides*, small amounts of this As species were also detected in one sample of the host mushroom, *Elaphomyces asperulus*. In a sample of another parasitic mushroom, *Ophiocordyceps sinensis*, arsenocholine-*O*-sulfate could not be detected, but the main species was another unknown compound that was oxidized to inorganic As(V) with hydrogen peroxide. This is the first discovery of arsenocholine-*O*-sulfate in nature. It is possible that it is present in many other organisms, at least in low concentrations, and just has not been detected there yet because of its unusual chromatographic behavior. The existence of arsenocholine-*O*-sulfate brings up questions again about the biotransformation pathways of As in the environment and the specific behavior of fungi.

Chemické složení plodnic jelenky drsné (ASP-059) a různých vzorků stromat housenice cizopasně

Unknown 1: arsenocholin sulfát





Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Speciation analysis of elements accumulated in *Cystoderma carcharias* from clean and smelter-polluted sites



Jan Borovička^{a,b,*}, Simone Braeuer^c, Jan Sácký^d, Jan Kameník^b, Walter Goessler^c, Jakub Trubač^e, Ladislav Strnad^f, Jan Rohovec^a, Tereza Leonhardt^d, Pavel Kotrba^d

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HIGHLIGHTS

- *Cystoderma carcharias* accumulates Cd, concentrations of up to 600 mg kg⁻¹ were found.
- Pollution influences element concentrations but only to some extent As speciation.
- As speciation of *C. carcharias* consists of many compounds, several are still unknown.
- Arsenobetaine is the main As species in *C. carcharias*.
- Cysteiny-rich peptides are involved in Cd and Cu binding in *C. carcharias*.

GRAPHICAL ABSTRACT

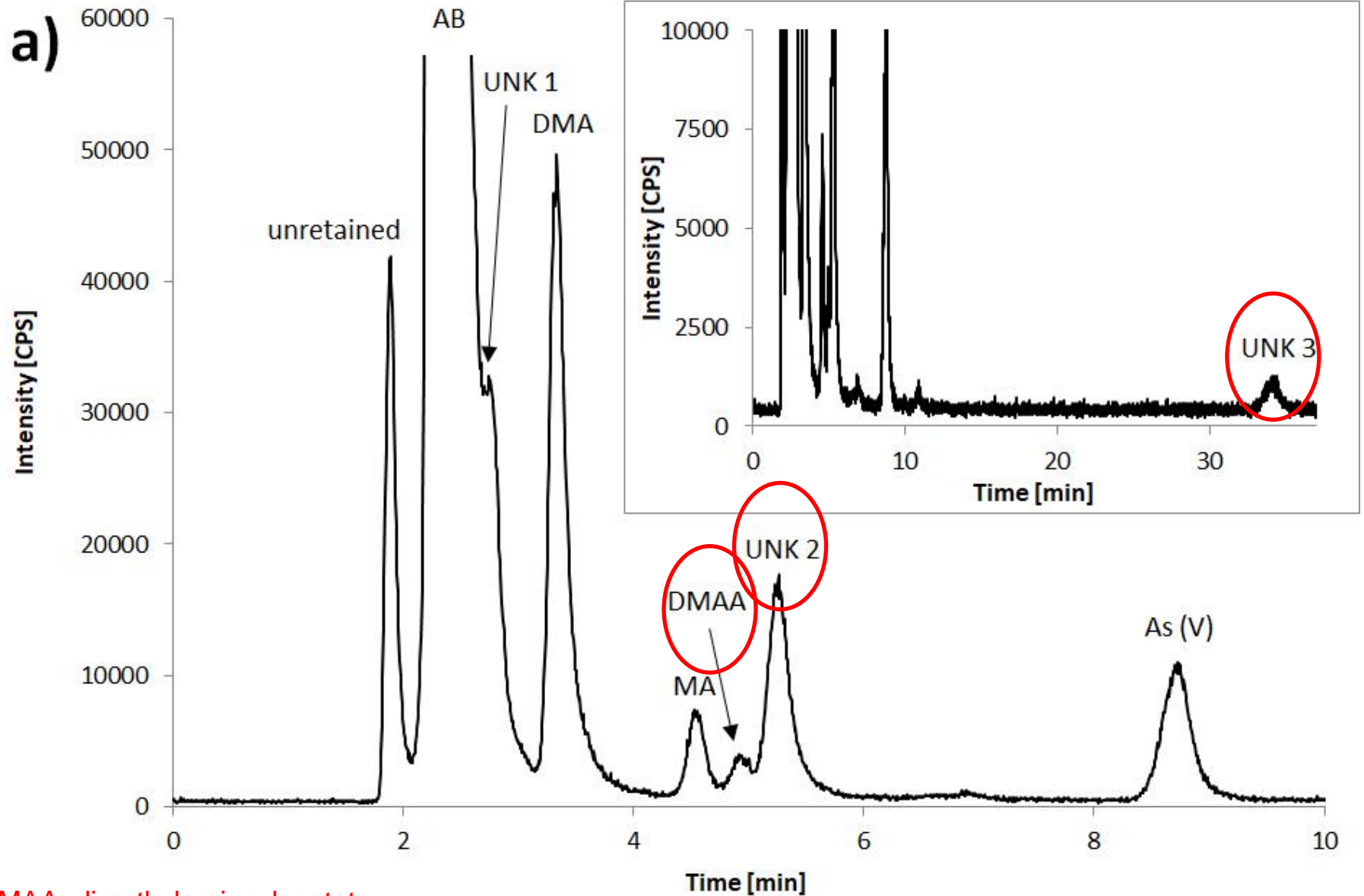


a



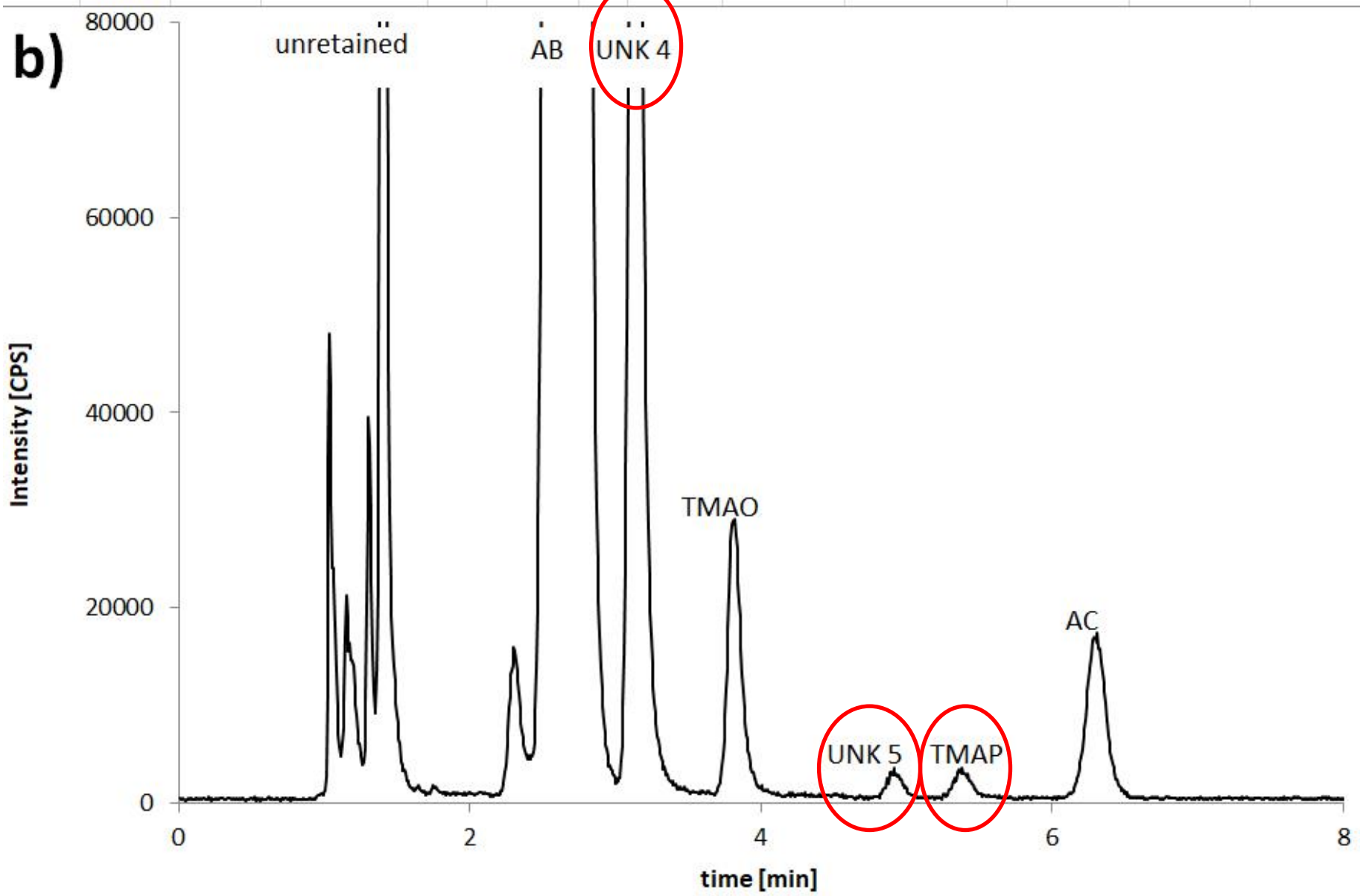
Zrnivka žraločí – *Cystoderma carcharias*

anion-exchange chromatogram

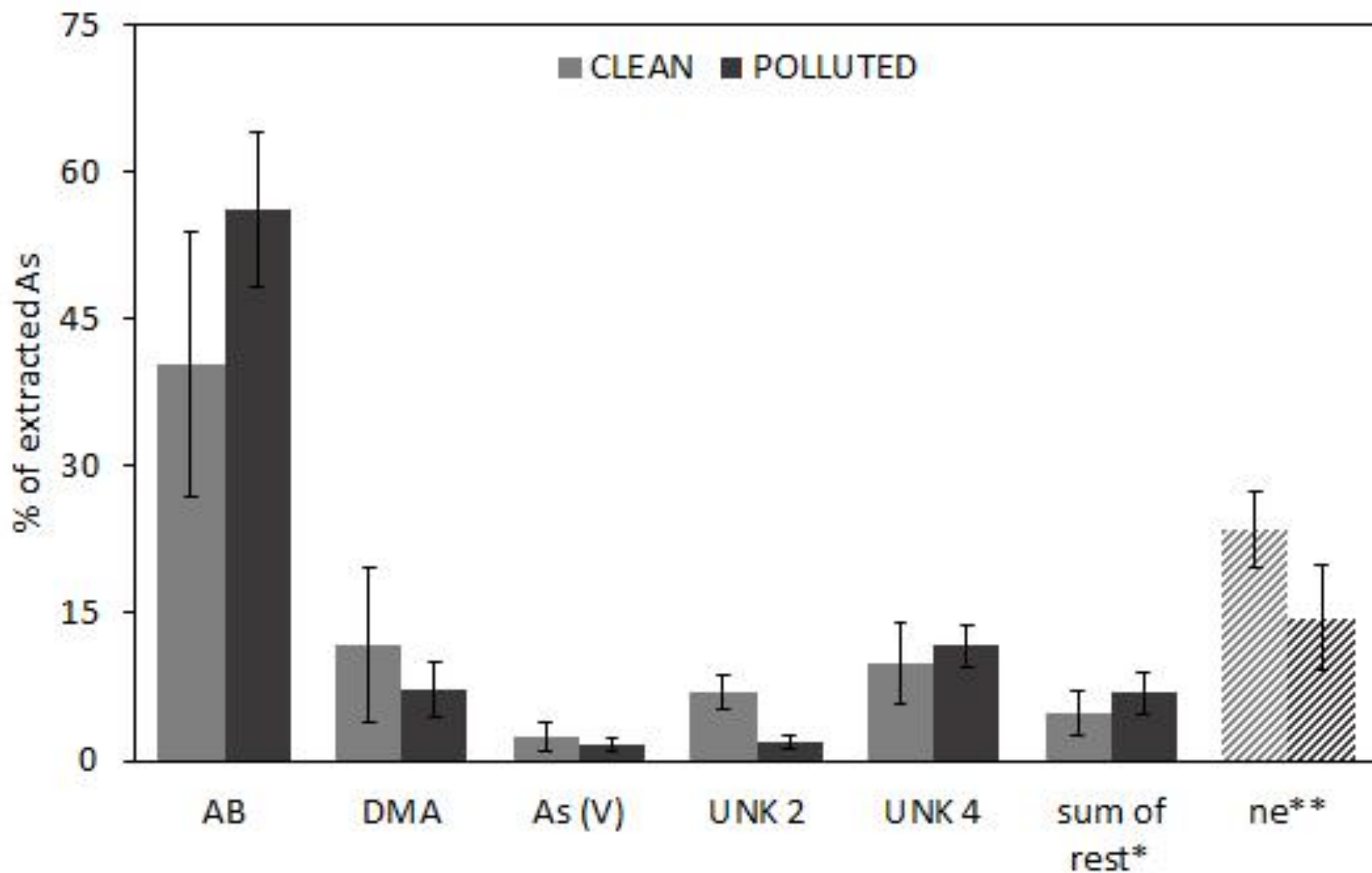


DMAA: dimethylarsinoylacetate

cation-exchange chromatogram



As a jeho sloučeniny v *C. carcharias*





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Talanta

journal homepage: www.elsevier.com/locate/talanta



Homoarsenocholine – A novel arsenic compound detected for the first time in nature



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ARTICLE INFO

Keywords:

Arsenic speciation

Ramaria

Fungi

Homoarsenocholine

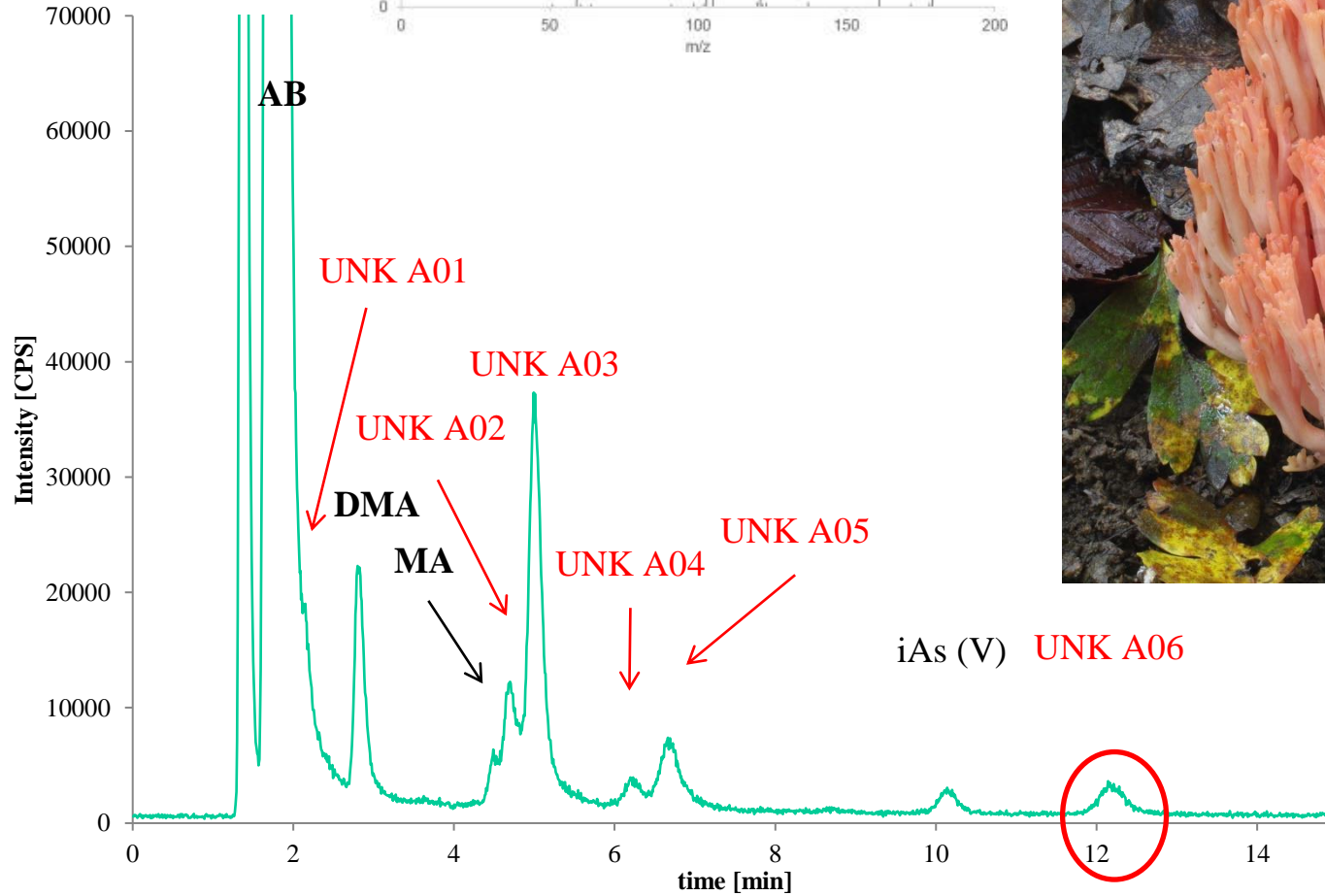
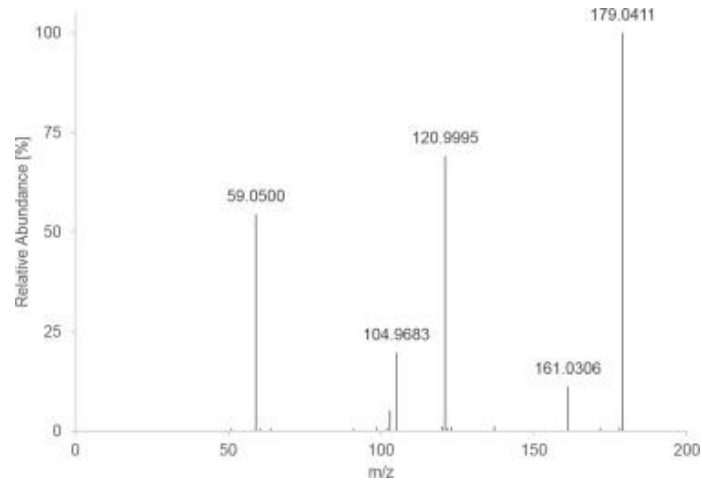
(3-hydroxypropyl) trimethylarsonium ion

ICPMS

ABSTRACT

The arsenic speciation was determined in macrofungi of the *Ramaria* genus with HPLC coupled to inductively coupled plasma mass spectrometry. Besides arsenic species that are already known for macrofungi, like arsenobetaine or arsenocholine, two compounds that were only known from marine samples so far (trimethylarsoniopropionate and dimethylarsinoylacetate) were found for the first time in a terrestrial sample. An unknown arsenical was isolated and identified as homoarsenocholine. This could be a key intermediate for further elucidation of the biotransformation mechanisms of arsenic.

Kuřátka lososová



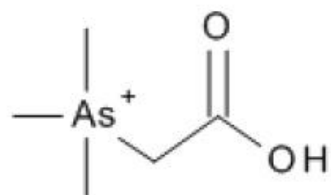


homoarsenocholin

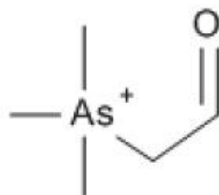
trimethylarsoniopropionate

Table 1 Total As and extracted As concentrations in *Ramaria* samples [$\text{mg kg}^{-1} \text{ dm}$] and detected As species [% of extracted As]. Other As species that were detected in small amounts (< 5 %) are: MA, DMA, As (V), TMAO, TETRA, DMAA and several unknown As species.

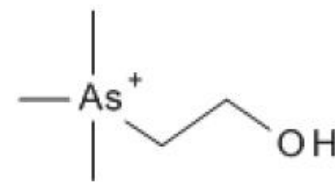
Sample ID	Species	origin	total As [mg kg^{-1}]	extr. As [mg kg^{-1}]	AB [%]	AC [%]	TMAP [%]	AC2 [%]
ASP-017	<i>R subbotrytis</i>	Slovakia	25 ± 2	22 ± 2	92 ± 7	1.6 ± 0.3	0.16 ± 0.02	0.27 ± 0.04
ASP-023	<i>R subbotrytis</i>	Czech Republic	61 ± 5	66 ± 4	91 ± 9	2.7 ± 0.4	0.3 ± 0.1	0.47 ± 0.02
ASP-068	<i>R subbotrytis</i>	Czech Republic	44 ± 4	39 ± 1	80 ± 20	1.7 ± 0.2	0.58 ± 0.01	0.47 ± 0.04
STM-107	<i>R sp.</i>	Austria	1.7 ± 0.1	1.4 ± 0.1	67 ± 2	4.1 ± 0.2	1.26 ± 0.1	0.82 ± 0.08
STM-108	<i>R sp.</i>	Austria	11.7 ± 0.2	9.5 ± 0.1	89 ± 1	1.57 ± 0.02	0.46 ± 0.02	0.37 ± 0.01
STM-109	<i>R sp.</i>	Austria	8.3 ± 0.3	6.9 ± 0.2	87 ± 2	2.4 ± 0.1	0.83 ± 0.03	0.93 ± 0.01



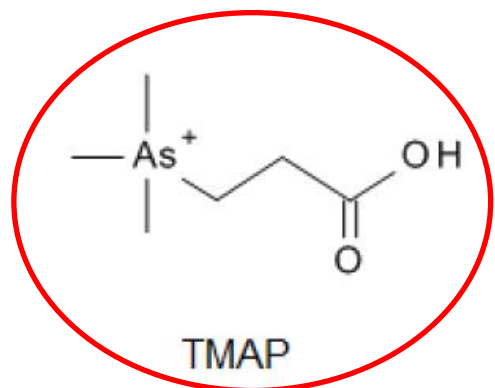
AB



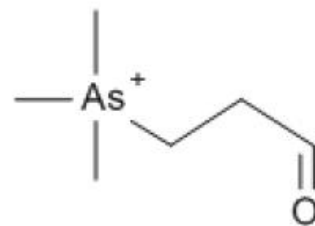
AB aldehyde



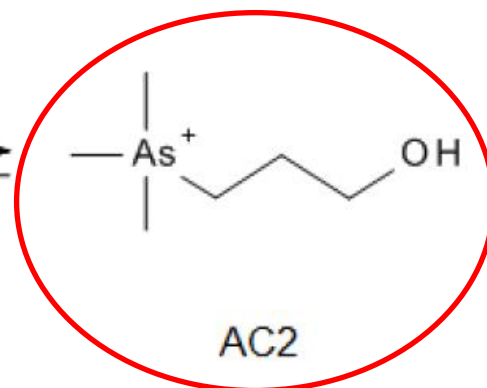
AC



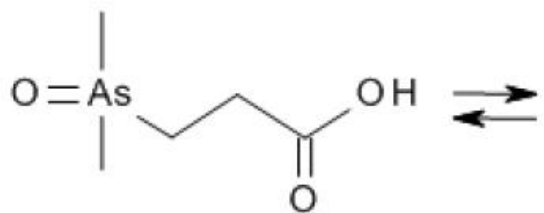
TMAP



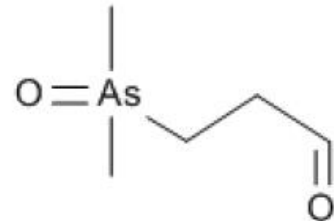
TMAP aldehyde*



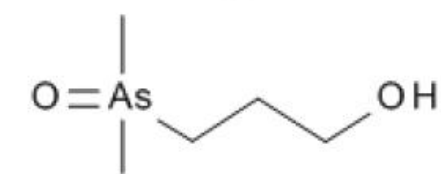
AC2



DMAP



DMAP aldehyde*



Dimethylarsenopropanol*



Hřib modračka – *Cyanoboletus pulverulentus*

Cyano

entus

SMOTLACHA - VEJRYCH

HŘIB (MODRÁK) SADNÍ NE
(*Boletus hortensis* Sm., *pulverulentus* O.
Rickenii Gramb.)

Klobouk 4-10-15 cm široký, zprvu polokulovitý, natý, svrchu obyčejně světle nebo tmavě i někdy plstnatý. Trubičky vysoké, ke třeni připojené, zprvu s otvůrkami drobnými, později rozšířenými, zdvořilými. Třeň 3-11 cm dlouhý, 2-3 cm tlustý, zprvu obyčejně dečkovitý, později válcovitý, na spodu zúžený, s dužninou na lomu zprvu žlutá, rychle mění barvu, později se opět odbarvuje. Výtrusný prach olivový eliptický. Vůně a chuť houby příjemná, nakyslá.

Je to houba jedlá; místy se sbírá k jídlu, ač silně třeň odvádí. Tento hřib roste v celé Evropě (symbiosa) a v písku, kdežto Kallenbach sbíral pod olšemi (nebylo zjištěno, zda byly v blízkosti). Zde ovšem všude má tvar poddoubníka a bývá velmi vonný. Zjistil jsem, že má podobně jako blízké druhy tvary. Jednak typický, jak jsem jej uvedl a jak je na obrázku (lipami nebo i jinde v lese, zvláště na straně severní, roste-li tento druh na plném slunci, pak je celý zelený zabarven (*Boletus lilacinus* Sm., hřib či modrák lilacinový) uprostřed obrázku). Roste-li však ve dvojitém stínu, pak je keřem a zároveň pod vysokou, stinnou lipou, pak jsou za mlada trubičky a nožka hned pod nimi žlutá (*Boletus citrinus* Sm., hřib či modrák citronový). Oba dva tvary mohou být omylem pokládány za samostatné druhy, ráni dužniny, které jest stejné u všech tří tvarů.

Jde. Je to stejné jako u *B. purpureus*. Pěstují si hřib sadní pod lipou na své zahradě na Záměcku u Hradce Králové. Zde jej také namaloval mistr Vejrych o prázdninách r. 1933. (Viz Časopis č. houbařů ročník XVIII./1938 a XXI.-1941 a „Přehled hub“). Tento druh přispěl k tomu, že jsem již ve svých pra-



50 DRUHŮ HUB
které doporučujeme sbírat

UNIE-PRAHA

Obr. 5 - Druh 5 - Velikost 1/1



stovky mg/kg As

1947

Cyanoboletus pulverulentus: otázky

- 1) Jaké
- 2) Je A
- 3) Jaká
- 4) Exist
- 5) Exist
- 6) Je hř

The image shows a screenshot of a Facebook group page for 'Houby' (Mushrooms). The central image is the cover of the journal 'Mykologický sborník' (Mycological Bulletin), issue 3-4/2015, Volume 92. The cover features a large, dense cluster of yellowish-orange mushrooms growing on a dark, textured rock surface. The journal title is in white serif font, with the subtitle 'Časopis českých houbařů' (Journal of Czech Fungists) below it.

On the left side, there is a sidebar menu with the following items:

- Houby (Public group)
- Diskuze (Discussions)
- Členové (Members)
- Události (Events)
- Videa (Videos)
- Fotky (Photos)
- Soubory (Files)
- Přehledy skupiny (Group Overview)
- Spravovat skupinu (Manage Group)

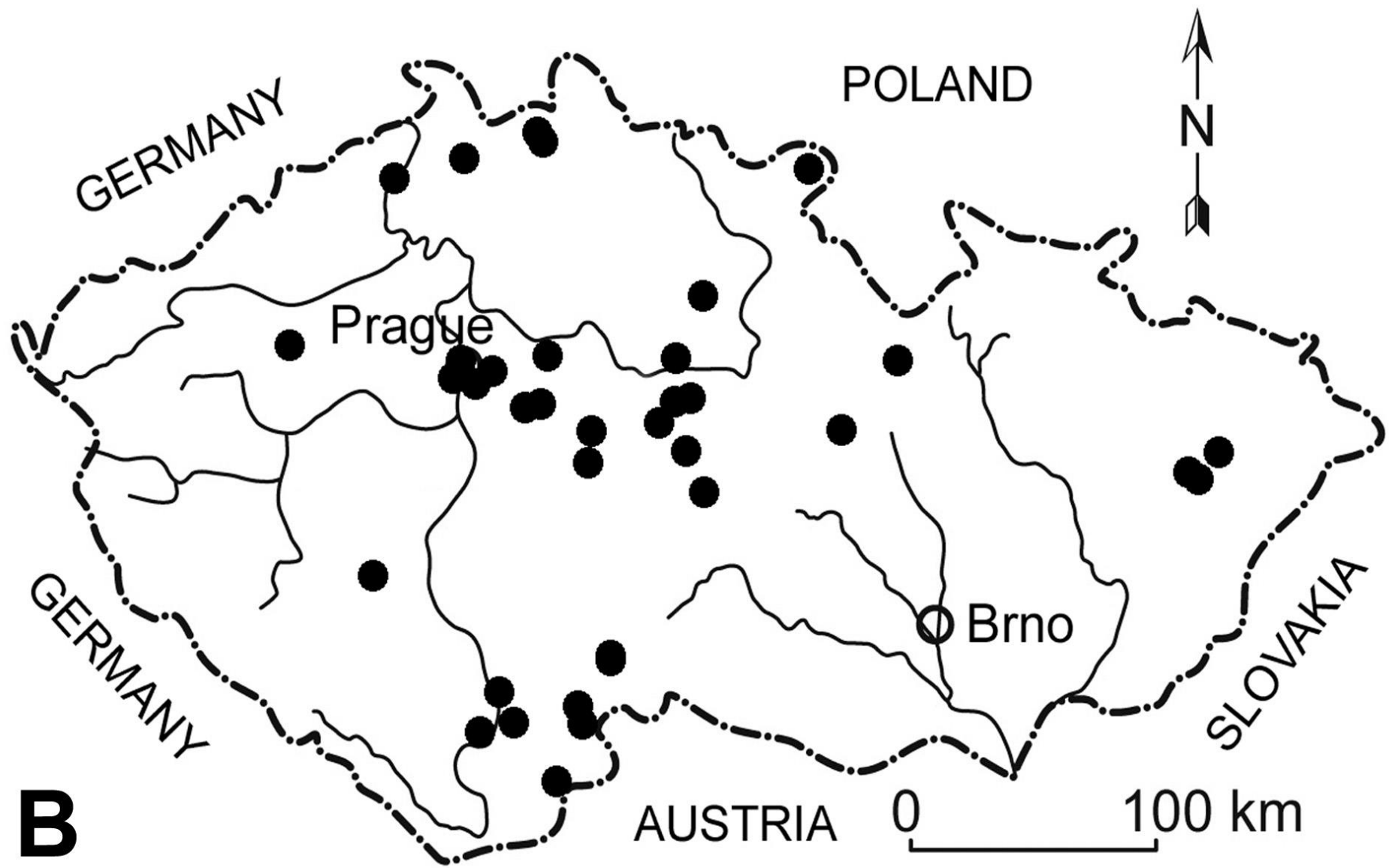
Below the menu is a search bar for the group's photos. Underneath, there is a list of representatives (Zástupci) for the group, including 'Ateisté ČR - uzavřen...' (1), 'Houby', 'Česká mykologická...' (20+), 'Ateisté' (13), 'MYKOLOGICKÁ P...' (20+), 'European Boletes' (20+), 'The Mushroom Ide...' (20+), 'Mediterranean Fungi' (20+), and 'Houby, hlenky, lišej...' (20+).

On the right side, there is a post from the group. The post header includes 'Změnit fotku skupiny' (Change group photo). The main text of the post reads: 'chozí. Prosíme, přečtete... (vpravo - Popis sku... bilu Informace o skupi... dodržujte. Děkujeme.' Below the text are several profile pictures of group members and buttons for 'Přidat člena' (Add member). At the bottom of the post, there are options to 'Upravit' (Edit), 'Přidat tagy' (Add tags), and 'Přidat klíčových slov' (Add keywords).

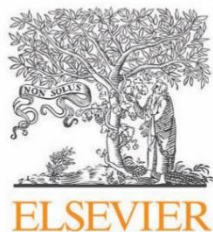


Česká republika (35)
Francie (1)
Madeira (1)
USA (1)

Cyanoboletus pulverulentus



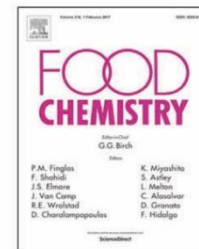
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Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem



Arsenic hyperaccumulation and speciation in the edible ink stain bolete (*Cyanoboletus pulverulentus*)



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ARTICLE INFO

This paper is dedicated to Tjakko Stijve on the occasion of his 80th birthday.

Keywords:

Edible mushrooms
Dimethylarsinic acid
Soil
Health risk
HPLC-ICPMS

ABSTRACT

The edible ink stain bolete (*Cyanoboletus pulverulentus*) was found to hyperaccumulate arsenic. We analyzed 39 individual collections determined as *C. pulverulentus*, mostly from the Czech Republic. According to our results, concentrations of arsenic in *C. pulverulentus* fruit-bodies may reach 1300 mg kg^{-1} dry weight. In most collections, data for total and bioavailable arsenic in underlying soils were collected but no significant correlation between the soil arsenic content and arsenic concentrations in the associated fruit-bodies was found. Within the fruit-bodies, we found the majority of arsenic accumulated in the hymenium. Besides occasional traces of methylarsonic acid (MA), the arsenic speciation in all mushroom samples consisted solely of dimethylarsinic acid (DMA) and no inorganic arsenic was detected. Because of the carcinogenic potential of DMA, *C. pulverulentus* should not be recommended as an edible mushroom and its consumption should be restricted.

VÝSLEDKY

1) Vysoké rozpětí koncentrací As v plodnicích:

2.4 – 1300 mg/kg

Průměr a SMODCH: 250 ± 260 mg/kg

Medián: 160 mg/kg

= jedná se skutečně o jeden druh, nebo je ta variace způsobená jinými faktory?

VÝSLEDKY

Jak je to s druhy: existuje v datasetu více modraček?

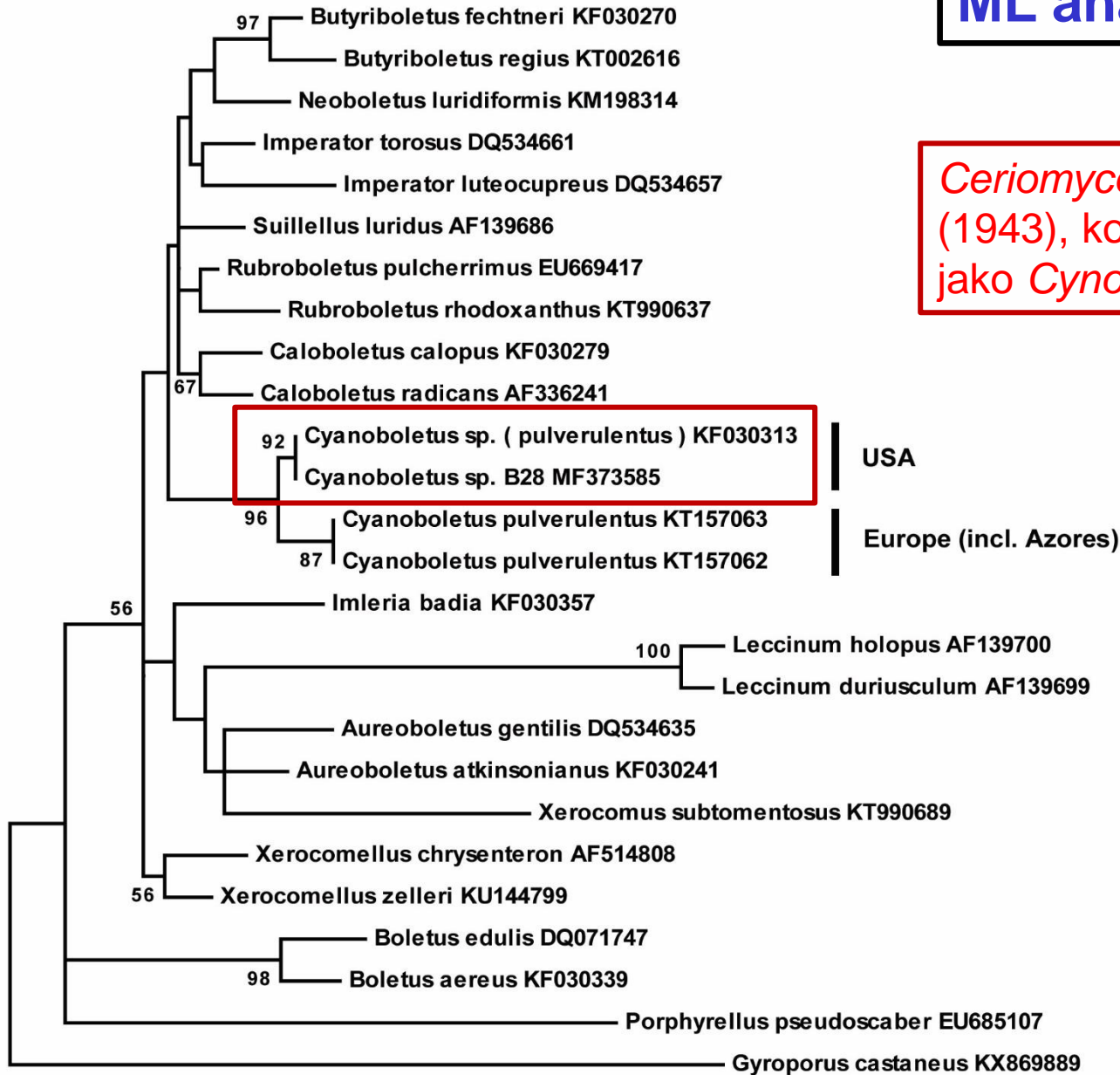
ITS rDNA pro šest evropských kolekcí identická

Americký sběr odlišný
(sekvence LT714710, 86% podobnost)

Do jakého rodu patří?
Je to *Cyanoboletus*?



ML analýza (LSU rDNA)

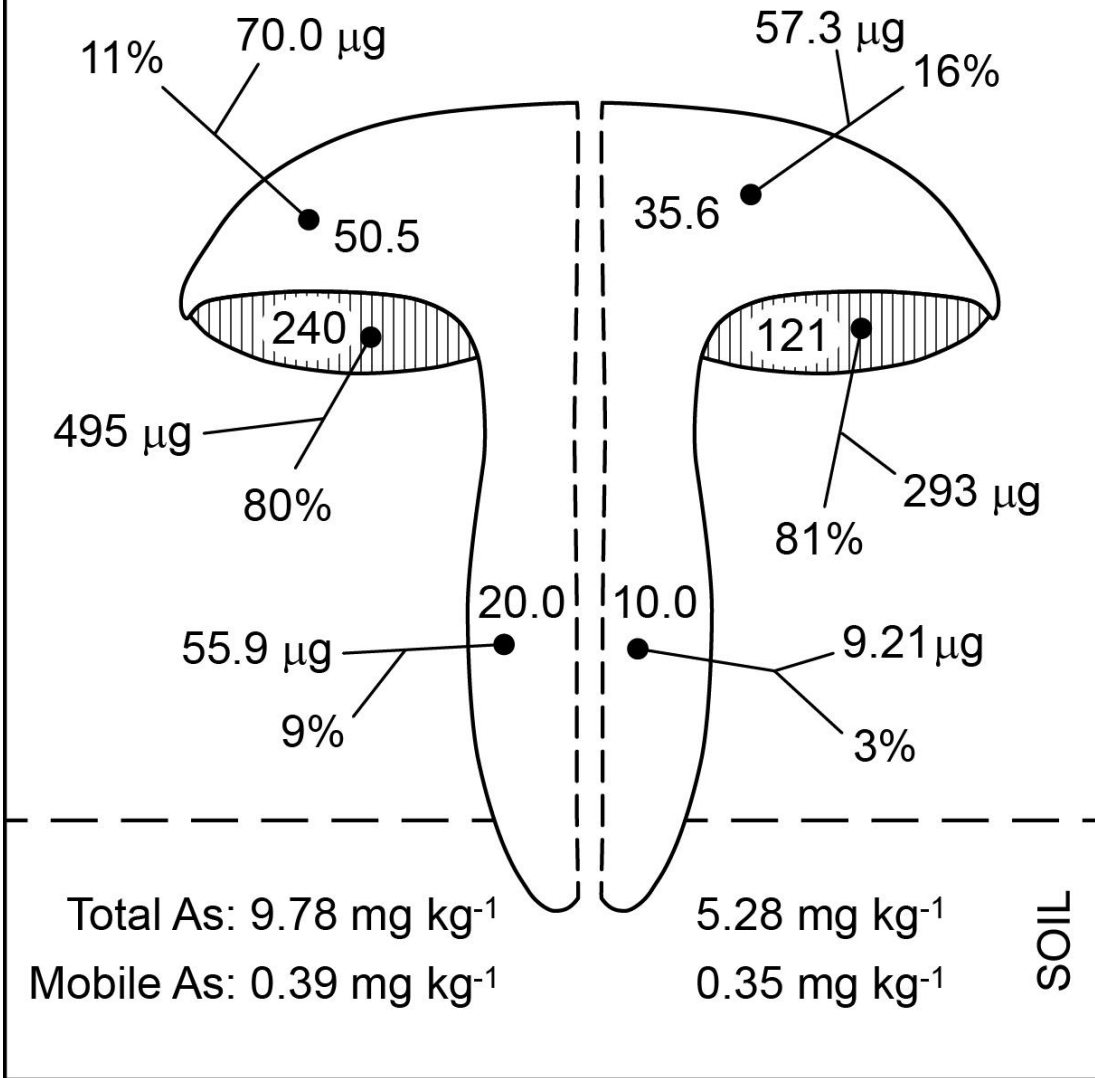


Ceratomyces cyaneitinctus Murrill (1943), kombinován v roce 2021 jako *Cynoboletus cyaneitinctus*.

0.02

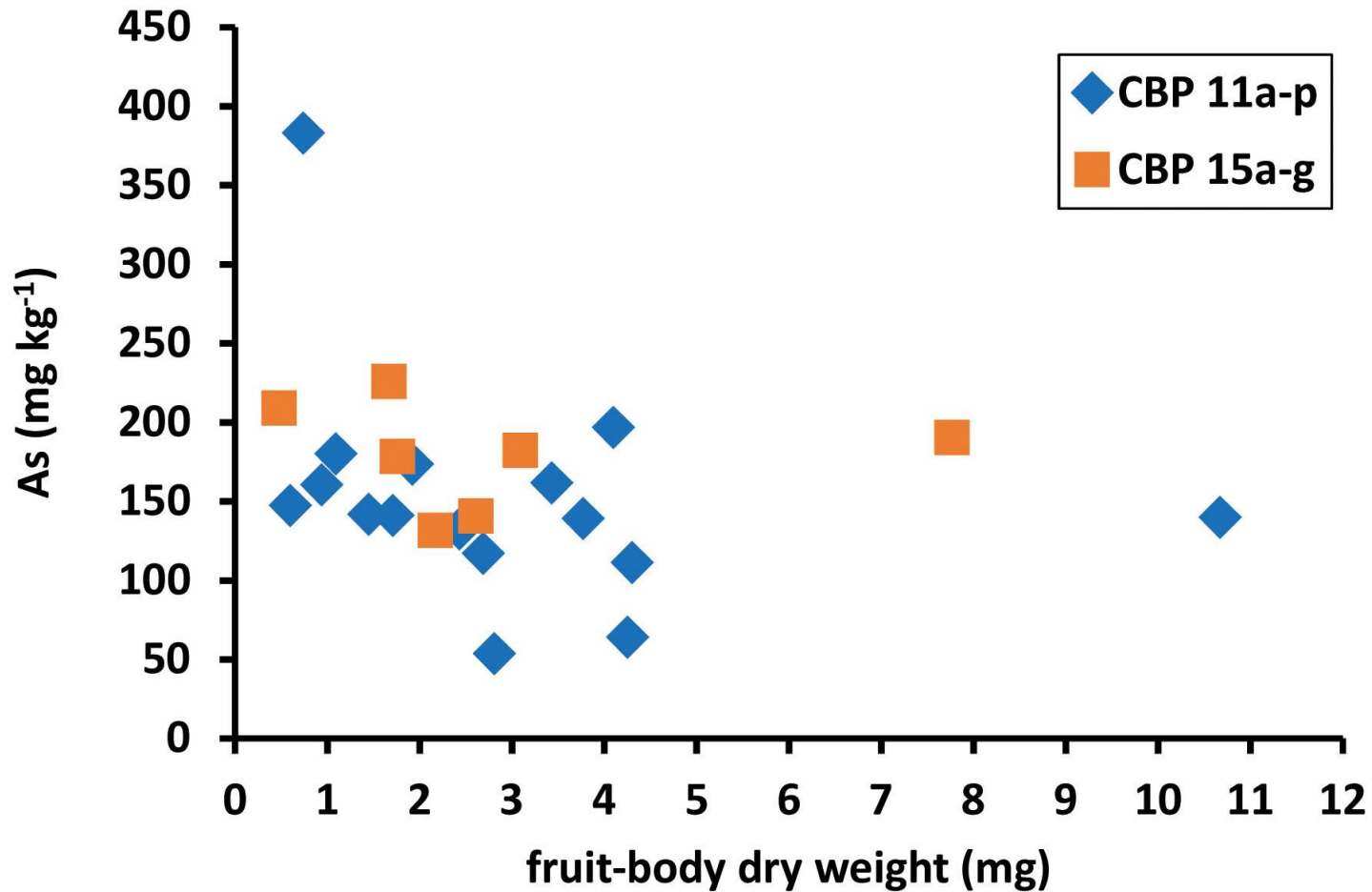
CBP-10b
As: 99.6 mg kg⁻¹

CBP-25b
As: 72.7 mg kg⁻¹

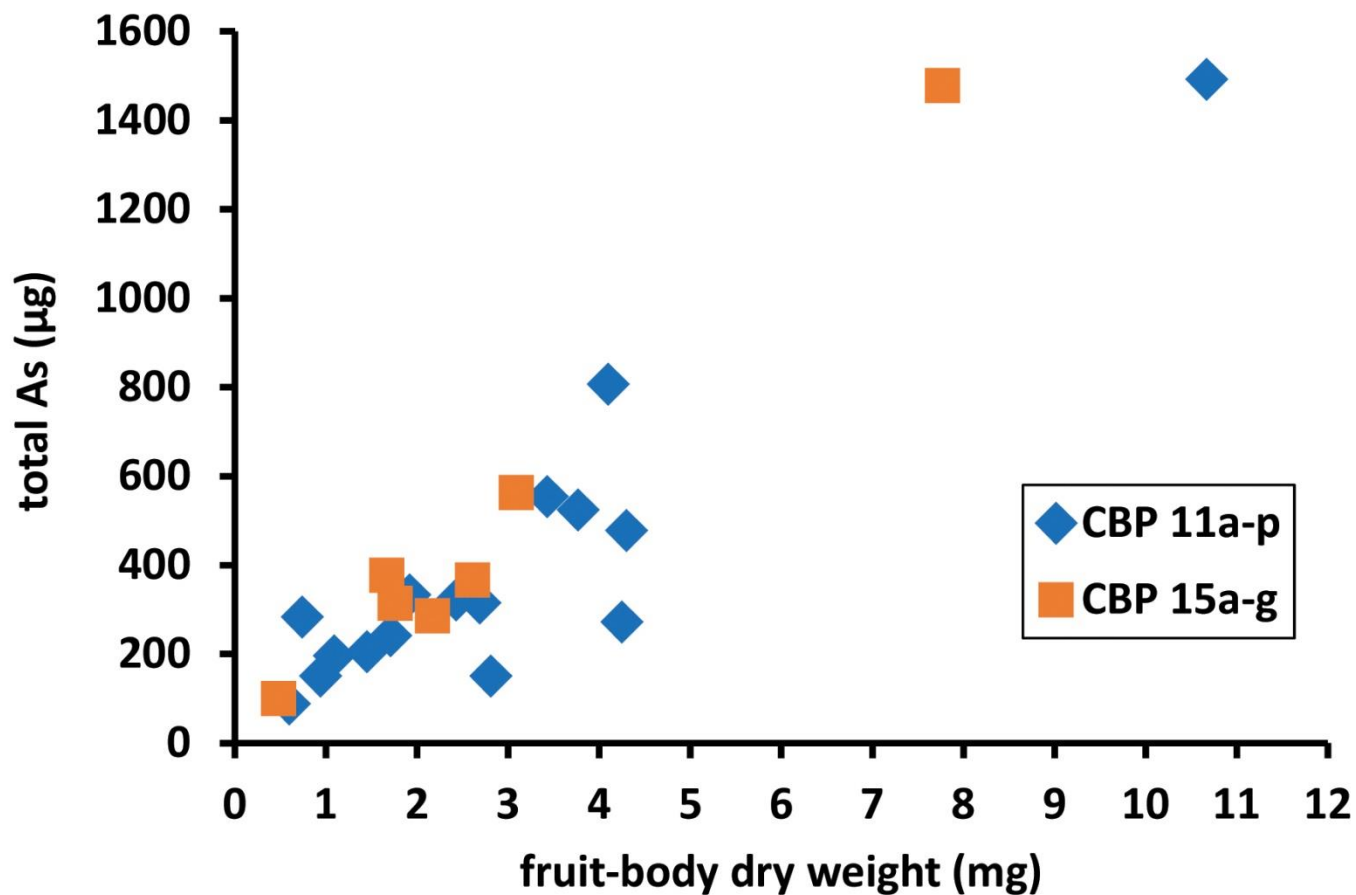


Dvě plodnice
Dvě podobné lokality
Podobné koncentrace
Stejná distribuce

Koncentrace As / hmotnost plodnice



Celkové množství arzénu / hmotnost plodnice



VÝSLEDKY

C. pulverulentus preferuje kyselé půdy (Ah horizont), s pH (H₂O) v rozmezí 3.6–7.0 (medián 5.1).

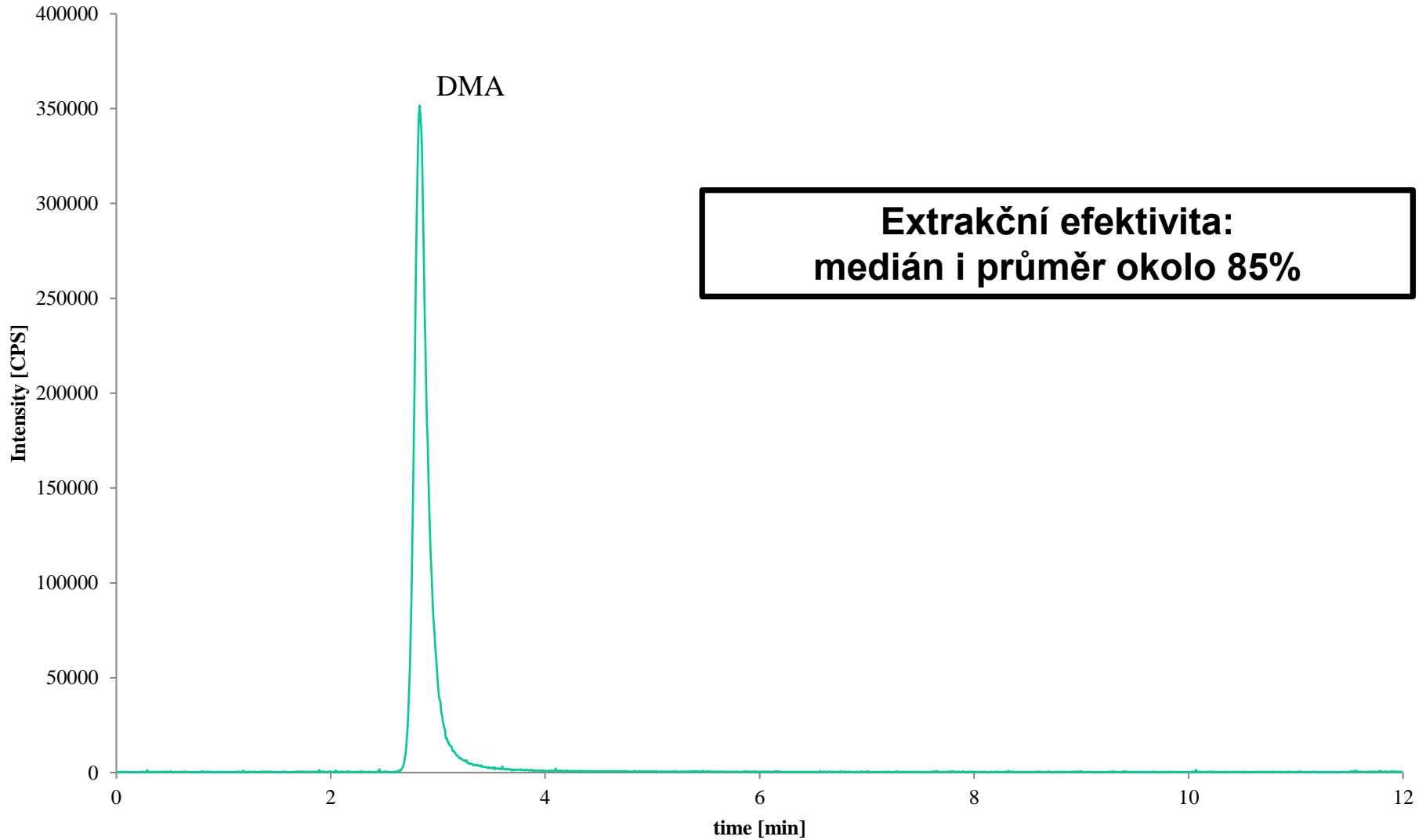
As v půdách (Ah): 6–35 mg/kg
(medián 12.2 mg/kg).

Nebyla nalezena významná závislost mezi koncentrací As v půdách (celkový / biodostupný arzén) a koncentrací v plodnicích modraček.



Jen a pouze DMA*

*se stopami MA v několika kolekcích



VÝSLEDKY



DMA: látka s nízkou akutní toxicitou, ale

➔ pravděpodobně karcinogenní (United States Environmental Protection Agency)

➔ jednoznačně karcinogenní (International Agency for Research on Cancer)

European Food Safety Agency:

zhodnocení rizika karcinogenních substancí pomocí kalkulace MoE: Margin of Exposure, mezní expozice

VÝSLEDKY

70 kg těžká (lehká)
osoba

běžná koncentrace As v
plodnici (115 mg/kg)



**Konzumace více než 90 g
čerstvé houby ročně
teoreticky zvyšuje riziko
vzniku rakoviny.**

Takže je to na vás...

Záhada baňky velkokališné



Is arsenic responsible for the toxicity of the hyperaccumulating mushroom *Sarcosphaera coronaria*?



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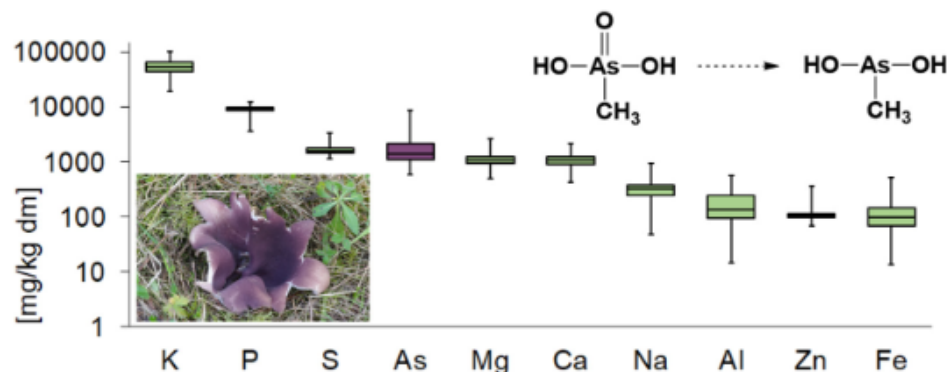
^c Nuclear Physics Institute of the Czech Academy of Sciences, Hlavní 130, 25068 Husinec-Řež, Czech Republic

^d Sentier de Clies 12, 1806 St. Léger, Switzerland

HIGHLIGHTS

- Arsenic accounts for up to record breaking 0.89% of dried *Sarcosphaera coronaria*.
- No correlations between arsenic in soil and fungal fruit-bodies from Czech Republic.
- Methylarsonic acid accounts for >90% of the total arsenic in fruit-bodies.
- Significant concentrations of highly toxic methylarsonous acid in fruit-bodies
- Arsenic could be responsible for the toxicity of *Sarcosphaera coronaria*.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 10 March 2020

Received in revised form 12 May 2020

Accepted 16 May 2020

Available online 22 May 2020

Editor: Filip M.G. Tack

Keywords:

Crown Cup

ICPMS

Arsenic speciation

Poisoning

Soil

Methylarsonous acid

ABSTRACT

The Violet Crown Cup, *Sarcosphaera coronaria*, is a rather inconspicuous mushroom, but with an interesting and unresolved mystery. In earlier days, the mushroom was considered edible, but several poisonings were reported in the early 20th century. The reason for the seemingly sporadic toxicity of *S. coronaria* is still unknown. One possible explanation is arsenic, since Crown Cups can take up high amounts of this element. We investigated the arsenic concentration and arsenic speciation in *S. coronaria* with inductively coupled plasma mass spectrometry (ICPMS) and HPLC coupled to ICPMS and found up to incredible 0.9% As (dry mass). Most of it was present as methylarsonic acid (MA), a less toxic form of this element. However, low concentrations of the highly toxic methylarsonous acid [MA (III)] were also detected. The amounts were too low to pose an acute risk for consumers, but the concentration of MA (III) significantly increased during simulated gastric digestion. We could not unambiguously identify arsenic as the toxic constituent of *S. coronaria*, but we demonstrated that the extremely toxic MA (III) can be formed under certain circumstances, which should be carefully investigated in future.

Baňka veľkokališná – *Sarcosphaera coronaria*





Table 3. As concentrations (mg kg^{-1} dry mass) in *Sarcosphaera coronaria*, reported by various authors. n = number of samples; n.a. = not available. *Reported as 15 mg kg^{-1} (fresh mass basis).

Year	Origin	n	Mean	range	Source
1990	Switzerland	4	872	360 - 2130	(Stijve et al., 1990)
1995	Switzerland, Slovenia	3	877	150* - 2120	(Byrne et al., 1995)
2001	Switzerland	15	647	248 - 2410	(Stijve, 2001)
1997, 2003, 2006	Italy	17	> 1000	153 - 3160	(Cocchi, 2003; Cocchi et al., 2006; Cocchi and Vescovi, 1997)
2004	Czech Republic	1	7090	-	(Borovička, 2004)
2007	Turkey	1	8.8	-	(Konuk et al., 2007)
2008	USA, CA	n.a.	610	n.a.	(Stijve, 2008)
2020	Czech Republic	62	1800 ± 1500	380 - 8900	This work
2020	Northern America	9	33 ± 36	3.2 - 120	This work

Table 4. As concentrations (in mg kg⁻¹ dry mass) in soil (mean ± standard deviation of three samples) and corresponding *Sarcosphaera coronaria* samples (mean ± standard deviation of all samples from the same site), and the calculated bioaccumulation factor (BAF = mushrooms/soil)

Sample	Soil	<i>S. coronaria</i>	BAF
ASP-045	6.8 ± 0.12	8900	1310
ASP-127	22 ± 1.2	1200 ± 300	55 ± 14
ASP-128	15 ± 0.46	2200 ± 800	150 ± 50
ASP-129	17 ± 2.6	1800 ± 320	110 ± 20
ASP-130	16 ± 0.74	1300 ± 240	83 ± 15
ASP-131	16 ± 0.65	1100 ± 480	68 ± 30
ASP-132	48 ± 0.47	3820 & 3510	79 & 72
ASP-133	37 ± 0.98	1600 ± 430	43 ± 12
ASP-134	12 ± 0.46	4100 ± 2400	340 ± 200
ASP-135	13 ± 0.56	2900 ± 530	230 ± 40
ASP-178	22 ± 1.2	670 ± 380	31 ± 17
ASP-179	10 ± 0.24	1400	141
ASP-180	13 ± 0.1	790	59
ASP-142	6.6 ± 0.3	29 ± 5.9	4.4 ± 0.9

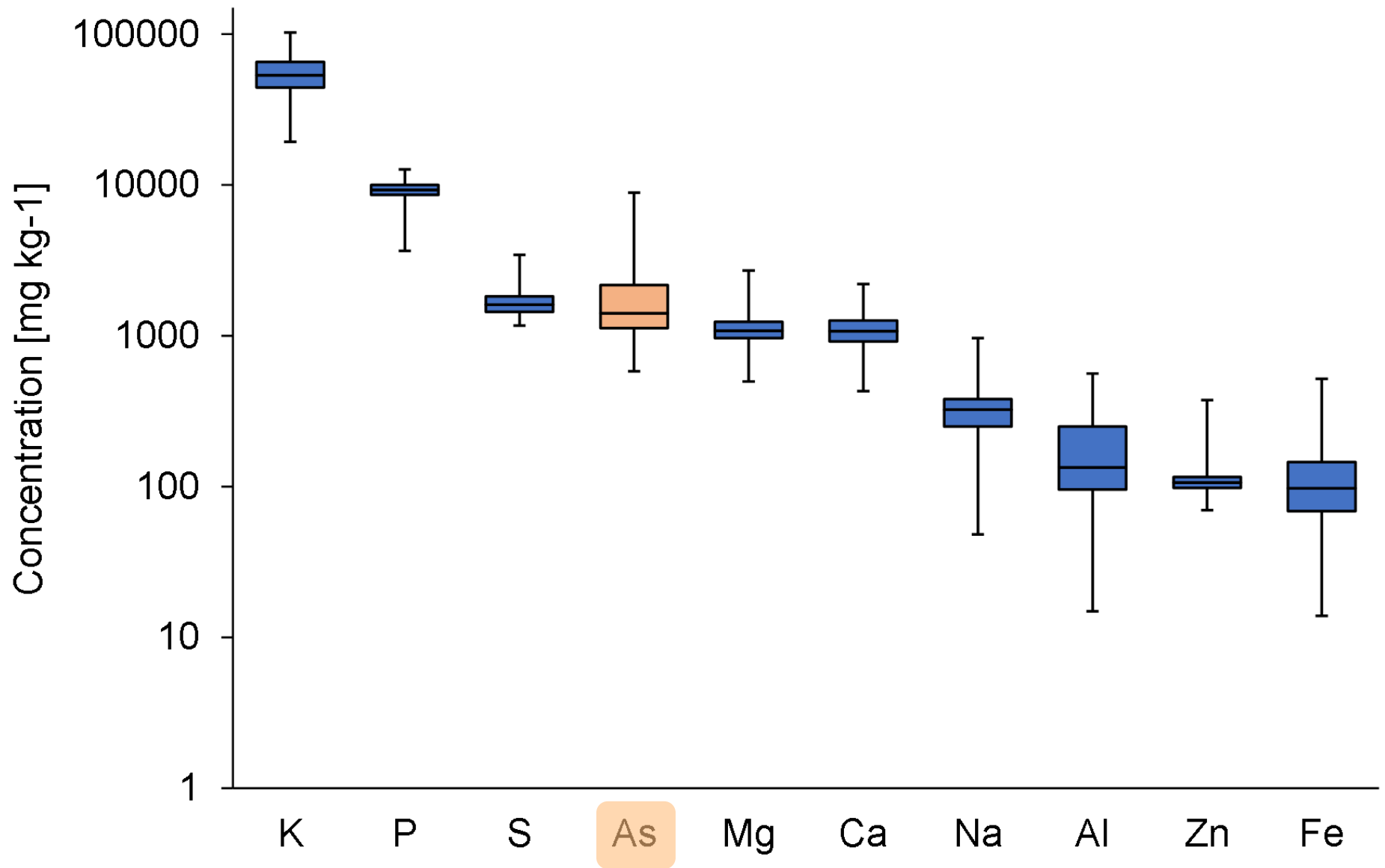
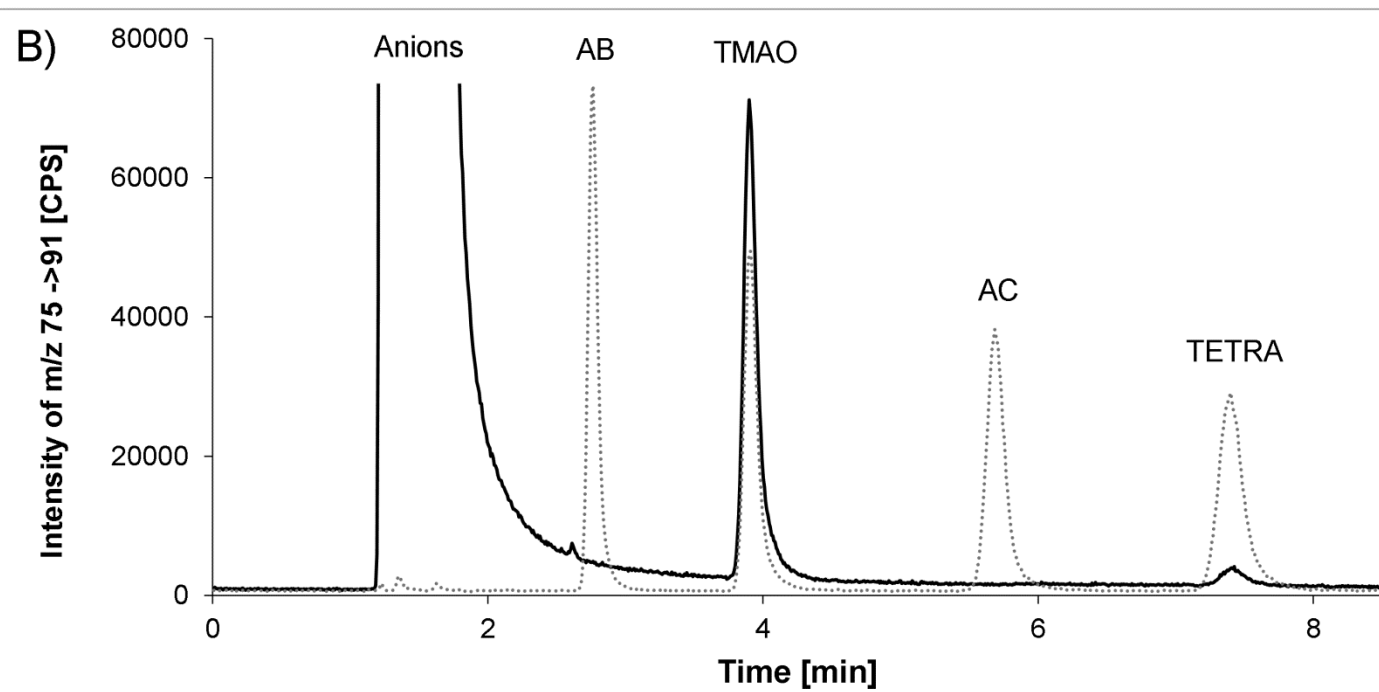
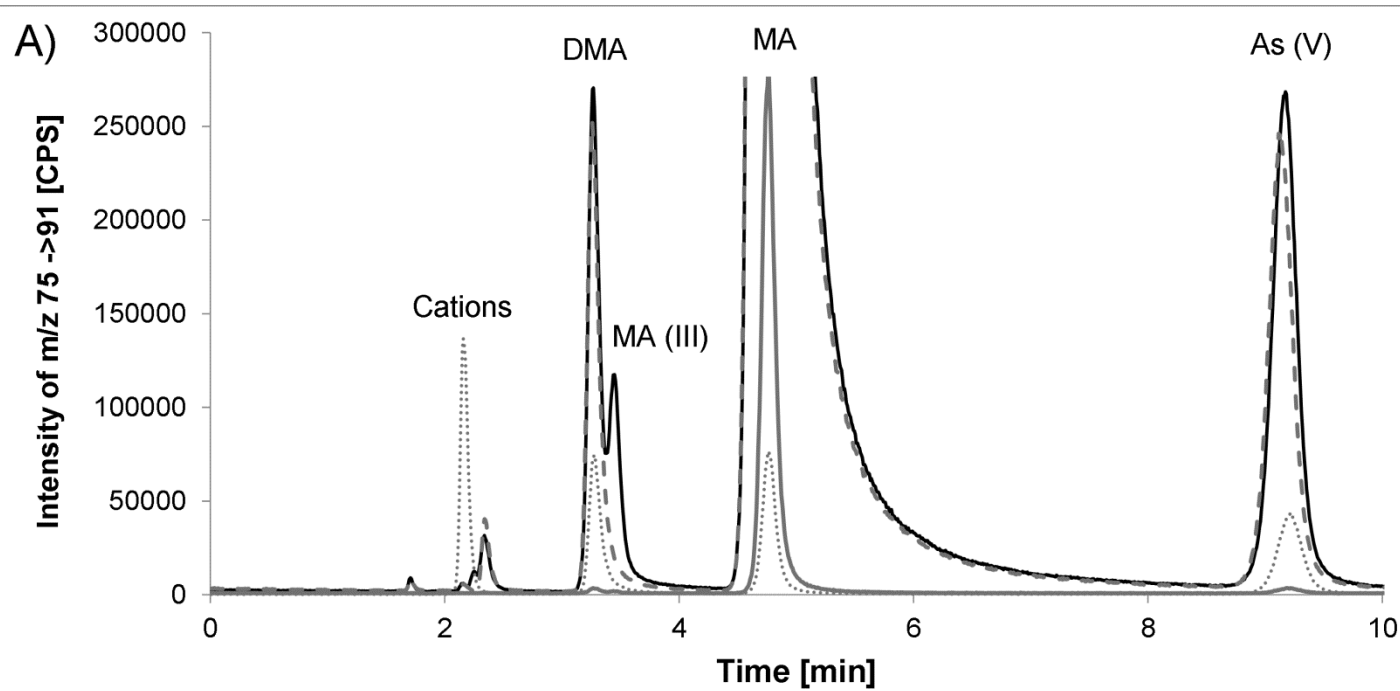


Table 5. As species in *Sarcosphaera coronaria* samples from the Czech Republic (CZ) and Northern America (NA), in % of total As. Traces = between 0.005 and 0.015 mg As kg⁻¹. n.d. = not detected (LOD: 0.005 mg As kg⁻¹). Not detected in any sample: AB, AC, DMAA, TMAP, AC2. “Not found as species” = Extracted As minus sum of all species. “Not extracted” = Total As concentration minus extracted As.

toxická

Species	Mean ± standard deviation [%]		Median [%]		Range [%]	
	CZ	NA	CZ	NA	CZ	NA
	MA	85 ± 13	77 ± 7.5	83	74	51 - 120
MA (III)	0.15 ± 0.19	1.9 ± 2.4	0.1	0.36	0.0002 - 1.1	0.066 - 6.9
DMA	0.25 ± 0.24	0.46 ± 0.23	0.17	0.49	0.027 - 0.98	0.17 - 0.91
iAs	0.52 ± 0.44	0.11 ± 0.10	0.49	0.094	0.001 - 2.1	n.d. (n=3) - 0.23
TMAO	0.06 ± 0.15	traces	0.02	traces	0.0018 - 1.1	n.d. (n=4), traces (n=5)
TETRA	0.006 ± 0.015	n.d.	0.0021	n.d.	traces (n=28) - 0.11	n.d.
Not found as species	12 ± 12	6.8 ± 3.8	16	7.3	≤ 41	≤ 11
Not extracted	1.3 ± 7.6	14 ± 6	1.5	14	≤ 22	8.6 - 27



Může trávení zvýšit podíl vysoce toxické MA (III)?

Table 6. Simulation of gastric digestion of *Sarcosphaera coronaria* sample ASP-045, in % of the control sample. The values are the average of two independent replicates, which always differed less than 10 % from each other.

Duration	MA	MA (III)	DMA	As (V)	TMAO	TETRA
1 hour	110	260	115	210	95	100
2 hours	115	290	120	205	110	130
4 hours	125	405	130	210	105	140
12 hours	115	440	110	220	119	132

ZÁVĚR

Koncentrace As v baňce velkokališné mohou dosáhnout až 0,9% v sušině. Plodnice ze Severní Ameriky mají koncentrace výrazně nižší (? jiný biologický druh).

Hlavní sloučeninou As v baňce je MA, byla zjištěna i její vysoce toxická forma MA (III), ale v malém množství.

Toxicitu baňky není možné vysvětlit vysokým obsahem As, nelze však vyloučit vliv kuchyňského zpracování či dalších faktorů.