Evaluation of arsenic occurrence in agricultural soils of the Bohemian Forest region

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Abstract

The aim of this study was to evaluate arsenic content in the soils of the Bohemian Forest (Šumava Mts.) region. Geogenic and anthropogenic factors of arsenic inputs into the soils were assessed. Arsenic concentration (2M HNO, and aqua regia extract) was determined in 221 soil samples collected in three Bohemian Forest districts (Klatovy, Prachatice, and Český Krumlov). More detailed results about the arsenic occurrence in soil samples were provided using various methods including assessment of arsenic distribution in soil profile, the sequential extraction procedure results or arsenic concentration ranged from 2.1 to 183 mg.kg⁻¹ in the non-forest soils of the region and followed an approximately lognormal distribution. Geometric mean concentration of aqua-regia-extractable arsenic is 10.9 mg.kg⁻¹. The results confirmed geogenic source of arsenic load in soils of the region, however, effects of anthropo genic factors could be raised in some parts of the region, especially because of the historical gold mining activities or urbanization factors. There was observed increased arsenic concentration in the zone stretched from Horská Kvilda to Velhartice inclusive primary gold deposits.

Keywords: arsenic, soil contamination, geogenic load, the Šumava Mts.

INTRODUCTION

Arsenic (As) belongs to the group of trace elements. It means that As concentration exceeding the trace concentration level in the environment may lead to a toxic effect. Geochemical properties of As are very complicated because there naturally occur various chemical modifications of As in the environment, resulting from the amphoteric nature of As ions. Insoluble As sulphides are oxidized through the As-bearing rock weathering and thus arsenites and arsenates are produced. Arsenic naturally prevails in the form of arsenates in aerated soil; nevertheless another oxidative state (arsenites) may also occur under redox conditions (CUL-LEN & REIMER 1989). The limit values for As in the Czech agricultural soils are regulated by the Directive No. 13/1994 Coll. (CZECH MINISTRY OF ENVIRONMENT 1994).

Arsenic is a significant contaminant of soils and groundwater in many regions, the world's most serious As contamination issues concern the contamination of drinking water sedimentary aquifers especially in South East Asia (Bangladesh and West Bengal, India, Vietnam), Mexico and Argentina, or Great Hungarian Plains (SMEDLEY & KINNIBURGH 2002; ANAWAR et al. 2002; ROYCHOWDHURY et al. 2002). Average arsenic concentration in European topsoil is estimated at 7.0 mg.kg⁻¹ (STAFILOV et al. 2010) but a background concentration can significantly differ depending on soil condition (see natural arsenic concentration in soils of central Europe, Table 1, and in the soils of Au-enriched metallogenic zones, Table 2).

The differentiation of risky element sources in soils is essential prerequisite for a proper

Region	Concentration	Extract	Source			
Czech Republic (cambisols, gneiss)	16.0*) 2.76*)	total content 2M HNO ₃	Podlešáková et al. (1994)			
Germany	6–17	aqua regia	Bundes-Bodenschutzgesetz in Podlešáková & Němeček (1996)			
Austria	15	aqua regia	Danneberg in Podlešáková & Němeček (1996)			
Poland	0.8–9.1 2.1 ^{*)}	total content	Dudka & Markert (1992)			

Table 1. Natural background arsenic concentration (in mg.kg⁻¹) in soils of Central Europe.

*) geometric mean

Table 2. Total As concentration (mg.kg⁻¹) in soils of some Au-enriched metallogenic zones.

Region	Concentration	Source			
Ghana – Ashanti Au mine	189–1,025	Bowell et al.(1994)			
Brazil – Iron Quadrangle	20–2,000	DESCHAMPS et al. (2002)			
Poland – Złoty Stok	70–11,500	KARCZEWSKA et al. (2006)			
Czech Republic – Mokrsko	330-26,000	Fп.пррі et al. (2004)			
Czech Republic – Kašperské Hory	60-818	FILIPPI et al. (2004)			

evaluation of soil load, not only concerning the legislation system of limit values, but also in relation to environmental risks. In case of arsenic, the interference between geogenic and anthropogenic origin of increased As concentration can be found in the Czech soils. Studying the As soil contamination in the Czech Republic, the highest values of As concentration were registered in the immission-impacted zones with the highest scale of atmosphere pollution matter (NĚMEČEK et al. 1996). In the soils of the immission-poor regions As concentration of geogenic origin can occur. HoLUB (1997) quotes that the arsenic concentration ranges 20–50 mg.kg⁻¹ in soils of the Central Bohemian Pluton parent rocks but it can reach 1,000 mg.kg⁻¹ in ore rich zones. Increased As amount in gold bearing quartz veins of acid rocks as part of mesothermal mineral association in some metallogenic zones of the Bohemian Massif was discussed by FILLIPPI et al. (2004). The As concentration over 2,000 mg.kg⁻¹ was found by FILLIPI et al. (2004) in agricultural soils near the Mokrsko gold deposit.

There is no explicit differentiation of the prevailing pollution sources in the areas where pollution sources mutually coincide. Solving the question of the ratio of geogenic and an-thropogenic loads rests not only on the complex assessment of the spatial distribution of the soil substrates indicating geogenic soil loads, but also on the analysis of emission flows, the assessment of contaminant distribution in a soil profile and on the trace elements solubility assessment using various extraction procedures (NĚMEČEK et al. 1996; VÁCHA et al. 2002). The hazards flowing from geogenic load are generally regarded as lower than from anthropogenic contamination.

Geogenic load background in the region

Natural background concentration of risky elements is determined by the soil substrate character or by the metallogenic zones in the acid igneous and metamorphic rocks areas, hence, two categories of geogenic content are usually distinguished (VACHA et al. 2002).

Lithogenic As content is determined by a soil substrate. Arsenic is present in the continental crust at an average concentration of 2–5 mg.kg⁻¹, mainly in the form of inorganic arsenic compounds associated primarily with igneous and sedimentary rocks (CULLEN & RE-IMER 1989). As concentration varies due to the rock type and is equal to 2 mg.kg⁻¹ in granites, 1 mg.kg⁻¹ in sandstones and limestones, and 10 mg.kg⁻¹ in schist (PERTOLD 1998). The regional arsenic lithogenic enrichment can be observed in the Prášily pluton granites and in the gneiss of the Moldanubian Zone with the arsenic amount significantly (three times) higher than the Earth's Clarke value (BARNET et al. 1994). The lithogenic arsenic enrichment can be locally associated with the gneiss and quartzites (Sušice region – BARNET et al. 2000), the acid veinous igneous rocks (in the Volyně region – BARNET et al. 1999), with the Rastenberg granite (Knížecí Stolec Mt. – BRUNNEROVÁ et al. 1995), or with the migmatite (the Kvilda plains – BURDA et al. 1999).

Chalcogenic As concentration is determined by naturally occurring arsenic in the ore rich zones with mineralized reefs associated with acid igneous or metamorphic rocks. Arsenic occurrence in the ore veins is associated with a whole range of minerals depending on the type of mineralization. The increased As amount in gold bearing quartz veins of acid rocks are observed in the Bohemian Forest region and arsenopyrite belongs among the most abundant ore mineral of the gold bearing quartz vein system (PUNČOCHÁŘ 1992; FILIPPI et al. 2004; ŠREIN et al. 2008). The primary gold bearing mineralization including arsenopyrite accumulation is well documented from the Kašperské Hory deposit (PUNČOCHÁŘ 1992; BABŮREK et al. 2001) and Horská Kvilda (ŠREIN et al. 2008). The arsenic content in quartz veins is estimated at 450 mg.kg⁻¹, with anomalies reaching 750 mg.kg⁻¹ in the Kašperské Hory deposit (PUNČOCHÁŘ 1992). ŠREIN et al. (2008) surveyed the arsenic accumulation in gold bearing mineralization near Horská Kvilda, where arsenic concentration in quartz veins ranged from 21.2 to 5,650 mg kg⁻¹ (mean with standard deviation: 833 ± 1.714 mg kg⁻¹) depending on the arsenopyrite occurrence, whereas there were measured even arsenic concentrations in the mineral horizon of the soils $(63\pm8.7 \text{ mg}.\text{kg}^{-1})$. FILLIPI et al. (2004) studied the arsenic distribution in various soil profiles surrounding the primary zone of the deposit near the Suchý Vrch Mt. in central part of the Kašperské Hory deposit. Sampling sites in a natural soil environment untouched by mining yielded the average arsenic concentration of 60 mg,kg⁻¹. The samples taken from old surface mining works are characterized by higher arsenic concentration (maximum 818 mg, kg⁻¹ in the upper part of the B horizon of a forest soil) and uneven irregular soil profile distribution of As values (FILLIPI et al. 2004). The increased As contents caused by dispersion of primary ore during surface mining can be regarded as an anthropogenic contamination.

The anthropogenic inputs in the region

Anthropogenic activity has resulted in the widespread atmospheric deposition of arsenic from the burning of coal and the smelting of non-ferrous metals. Agricultural practice, floods and then load spreading round the mine dumps are other important sources of As contamination of soil (VACHA et al. 2002). Arsenic release in the oxidation zone of mined deposits can be regarded as regionally restricted in comparison to another primary anthropogenic As inputs such as fossil fuel and waste combustion or agriculture use of arsenic containing preparations.



Fig. 1. The average annual concentration of arsenic in the atmosphere measured at the sampling sites of Churáňov and Klatovy (immission limit = 6 ng.m⁻³; data source: http://portal.chmi.cz/files/portal/docs/uoco/ isko/tab_roc/tab_roc_CZ.html).

The mass of 105 g.ha⁻¹ is average annual arsenic input into the Czech soils – atmospheric deposition gets 83%, agriculture fertiliser application 13% (BENEŠ et al. 1994). Atmospheric deposition is regarded as the most significant anthropogenic pollution source regarding small spatial scale (macro regional, global scale), the effect of other sources is rising with geographical scale. For a long-term trend of average annual concentration of arsenic in atmosphere see Fig. 1, with the data sets from two measurement localities (the high mountain site of Churáňov and the town of Klatovy). However, the concentration seems to be low in comparison to another regions in the Czech Republic, arsenic input by dry and wet deposition must be regarded as another potential soil pollution source especially for the upper soil horizons.

Records of long-term metal atmospheric deposition were studied in the bottom sediments of the Bohemian Forest lakes (VESELÝ 2000a, b). Enhanced atmospheric deposition of arsenic evolved 700 years ago, peaked during the 20th century (especially in the period from 1956 to 1978), and the effect of direct atmospheric deposition was still evident in 1998 (VESELÝ 2000a, b). The decrease in arsenic concentration was observed with the depth in Plešné Lake, thus direct atmospheric deposition (especially precipitation) can be regarded as an important source of arsenic (VESELÝ 2000b). The wet atmospheric deposition indicators were observed at the regional sampling site of Liz (TESAŘ et al. 2000). From the assessment of the annual deposition of arsenic measured in the form of occult and bulk precipitation in the Bohemian Forest region (Churáňov and Liz in the hydrological years 1994–1999), one can conclude that especially the occult precipitation is indispensable delivery mechanism for various pollutants including arsenic because it has been surveyed that the cloud precipitation has been much more contaminated with As than bulk deposition (TESAŘ et al. 2000; Doušová et al. 2007).

Increased As concentration caused by dispersion of primary ore during surface mining can be regarded as an important locally embedded source of anthropogenic contamination. The gold mining wastes were usually irregularly spread around the gold mining workings during the late medieval period (the thriving period from the 13th to 14th century). Arsenopyrite in mining wastes was oxidized, secondary arsenic minerals have been produced (scorodite), a part of arsenopyrites weathering product is bound into soils (especially hydrous ferric oxide sorbents), a part is leached to groundwater, a part enters surface waters (subsequent accumulated in sediments of erosion gullies and especially in the river alluvium), and a part comes into the site biological cycle (plant arsenic uptake) (Holub 1997; FIL-LIPI et al. 2004; DRAHOTA et al. 2009).

The objective of this study is to investigate arsenic occurrence in the soil of non-forest areas of the Bohemian Forest region considering potential sources of arsenic in soils. Geogenic source of arsenic is supposed to prevail in the regional soils. Relatively low atmospheric pollution can contrast the impact of the isolated local pollution sources or enable studying the effect of the geological background. In the study region, the increased As concentration, caused by dispersion of primary ore during surface mining, is supposed to be the important locally embedded source of anthropogenic contamination of soils.

MATERIAL AND METHODS

The data resulted from chemical analyses of 221 soil samples collected in the Bohemian Forest districts (Klatovy, Prachatice, and Český Krumlov) during the period 1992–2009. Soil samples were taken with a non-metallic tool from topsoil or a divot horizon in the depth of 5–25 cm on the localities of the agricultural land use (arable land, permanent grassland). GPS localisation, site description and pedologic characterisation were accomplished (for the soil sample characterisation, see Fig. 2). Chemical measurements were performed in the central laboratory of the Research Institute for Soil and Water Conservation in Prague. Exchangeable soil pH (0.2 M KCl) and content of organic carbon by the modified Tjurin method (ZBIRAL 2002) were determined in the soil samples. Soil arsenic concentration was determined after decomposition using the aqua regia and 2 M HNO₃ extract by atomic absorption spectrometry with the hydride generation measurement mode. Certified reference materials CRM 7001 Light Sandy Soil and CRM 7003 clay-loamy soil were applied for quality assurance of analytical data. The measurement uncertainty of arsenic assessment was 20% and the detection limit was 0.5 mg As kg⁻¹ for both extracts. The statistical evaluation proved that approximately 80% of total arsenic concentration in soil was extracted by aqua regia.

Confrontation of the arsenic concentrations (HNO₃ extract/aqua regia) can be used for a preliminary assessment of arsenic mobility. The As solubility assessment using HNO₃ extract and total content determination was successfully used for the arsenic source distinction between geogenic load and anthropogenic load of immission or fluvial origin (VACHA et al. 2002). The significantly high arsenic concentration in aqua regia extract together with lower arsenic concentration in HNO₃ extract can indicate a significant contribution of the geogenic source of soil contamination (VACHA et al. 2002).

Arsenic concentration in soil was assessed using relevant limit values included in the Directive No. 13/1994 Coll. (CZECH MINISTRY OF ENVIRONMENT 1994). Nevertheless, the confrontation of arsenic concentration with limit values could not be sufficient for the environmental risk assessment. Some supplement observations were performed for the assessment of environmental consequences following the arsenic occurrence in soils. Arsenic concentration was assessed in the plants picked from selected soil samples sites. The plant sample composition depended on the site land use – the grass species mixture came from permanent grassland and crop plants from arable land. Arsenic concentration in two soil horizons were analysed in some soil samples to study the trends of arsenic concentration distribution in selected soil profiles. More detailed results about arsenic bounds in soil are provided with





Table 3. The characteristics of soil samples used for sequential extraction procedure.

Locality	ocality Land use		Substrate	C _{org}	pН	As (aqua regia)
Zhůří	Permanent grassland	Entic Podzol	Gneiss	2.79	5.25	28.2
Strunkovice nad Blanicí Arable land		Haplic Stagnosol	Polygenetic loams	1.60	5.60	8.0

Table 4. Elementary statistics of arsenic concentration in non-forest soils of the Bohemian Forest region.

Conc.*)	Ν	Mean	SD	GM	Median	Min.	Max.	LQ	UQ	Skewness	Kurtosis
C-As	221	15.4	18.6	10.9	9.9	2.1	183	6.3	18.8	5.0	34.7
V-As	216	2.1	2.3	1.4	1.1	0.4	20.1	0.7	2.6	3.3	17.7

^{*)} Conc. – concentration: C-As – aqua-regia-extractable As (limit value = 30 mg.kg⁻¹ according the Directive No. 13/1992 Coll.), V-As – As in the 2M HNO₃ extract (limit value = 4.5 mg.kg⁻¹ according the Directive No. 13/1992 Coll.); N – number of samples, SD – standard deviation, GM – geometric mean, Min. – minimum, Max. – maximum, LQ – lower quartile, UQ – upper quartile

using sequential extraction procedure (SEP) – analytical technique for the As fractionation consisting of selective extractants used in a sequence to determine individual As fractions in order of solubility of arsenic compounds. The ZEIEN & BRÜMMER (1989) SEP was used in this study; its operating procedure was described in NĚMEČEK et al. (1998) or WENZEL et al. (2001) in detail. Two samples with various characteristics (geographical and pedological) were chosen for the SEP application – the sample from the high mountain locality of Zhůří and from the Bohemian Forest foothills (Strunkovice nad Blanicí, Table 3).

The data were processed using the ArcGIS Geostatistical Analyst programme. The ordinary kriging method based on parameters of spherical variogram was used for spatial interpolation of arsenic concentration in soil. Arsenic concentration data had been transformed (logarithmic transformation) before the geostatistical assessment was performed. The kriged values were classified according to the 20th, 40th, 60th, and 80th percentile values derived from logarithmically transformed data sample. The indicator kriging was used to visualize the probability of exceeding of the limit value for arsenic concentration in soil according to the Directive No. 13/1992 Coll. (2 M HNO₃ extract, CZECH MINISTRY OF ENVIRONMENT 1994).

RESULTS AND DISCUSSION

The results of the arsenic concentration in the soil samples from the Bohemian Forest region are depicted in Table 4. Arsenic concentration followed an approximately lognormal distribution, and geometric mean concentration of aqua-regia-extractable arsenic was 10.9 mg.kg⁻¹.

The potential arsenic load sources were studied in consequence of the observed spatial distribution of arsenic concentration in agricultural soils of the area (Fig. 3). The studied area can be regarded as the deposition-poor region with marginal atmospheric deposition impacts. The locally based sources of anthropogenic load influence spatial variability of the arsenic concentration in agricultural soils of the area due to the regional character of this study.

Spatial distribution of the arsenic concentration indicates the significance of geogenic load attended by the impacts of historical gold mining activities. The arsenic concentration in agriculture soils of the area exceed the legislative limit values for agricultural soils in some cases (see Fig. 3), however, they do not reach the extremely increased values measured



Fig. 3. Arsenic concentrations in surface waters (MAJER & VESELÝ 2005), soils and plants (this study) within the region studied.

by FILLIPI et al. (2004) in the forest soils covering gold mining remnants in the Kašperské Hory deposit. The old mine remnants are usually covered by forest soils, where high portion of arsenic from the oxidation processes of arsenopyrite is trapped. The potential evolution of the site after forest changes (forest soil liming, deforestation, and agricultural use) should be examined and discussed (HoLUB 1997).

Spatial pattern of the arsenic concentration in the agricultural soils shows three areas of increased values. The most distinctive area of increased arsenic concentration can be identified in the zone stretched from Horská Kvilda to Velhartice. The famous historical gold deposits are included in this zone, namely the primary ore deposits at Kašperské Hory, Horská Kvilda, Hartmanice, Dolejší Těšov, Hory Matky Boží, and Velhartice. The less distinct areas of increased arsenic concentration can be observed in the Volyňka catchment and in the Trojmezí upland following the natural geologic background. The increased arsenic concentration is characteristic for the acid igneous rocks in the Volyně region, the lithogenic arsenic contents can be locally enhanced in the consequence of gold mineralization occurrence (Nihošovice, Volyně, and Čkyně). Another area can be related to the arsenic enrichment of



Fig. 4. The evaluation of arsenic occurrence in agricultural soils within the region studied.

acid igneous rocks in the Trojmezí upland. The increased effect of traffic emissions from the transit road No. I/4 also can locally influence the soil load in this area.

The enhanced anthropogenic input of arsenic into soils can be roughly detected using the confrontation of the arsenic concentrations (HNO_3 extract/total content). The increasing proportion value indicates anthropogenic share of the arsenic load, the proportion value xceeding 40% is rather characteristic for the imission load (VACHA et al. 2002). The proportion values for the samples exceeding the legislative limit values are depicted in Fig. 3 (red labelled points). The increased proportion values can be observed in the Lipno region, where the increased solubility and profile distribution of arsenic can indicate influence of anthropogenic inputs via atmospheric deposition.

The profile distribution (two horizons) of arsenic was assessed for 25 selected soil profiles in the region (see Fig. 4). The profile distribution assessment can assist the risky element source identification (VACHA et al. 2002). The soils with geogenic load are characteristic in the element concentration gradation with the profile depth (for example see the soil profile trends in the first zone of the arsenic increased concentration in the western part of the region). The interesting results of the element distribution were obtained in the soil profiles in the Lipno region. The aqua-regia-extractable As concentration diminish with the soil depth whereas the potential mobile arsenic contents (HNO₃ extract) rise. This finding deserves



Fig. 5. The comparison of results of sequential extraction procedure among the regional samples (Zhůří and Strunkovice nad Blanicí) and the type samples for various sources of arsenic concentration in soil (Klínovčík, Litávka, Mikulov, and Kaňk – see the text for details).

more exploration. We assume that this could be caused by the soil (redox) conditions or by the soil horizons blending in consequence of soil tillage.

More detailed results about the arsenic bounds in soil are provided using the sequential extraction procedure. Fig. 5 compares the results of the As fractionation using sequential extraction procedure among two soil samples from the area and the type samples for geogenic (Klínovčík), fluvial (Litávka alluvium), imission (Mikulov) arsenic load, and the load spreading round the mine dump (Kaňk). The As association with crystalline Fe oxides (due to primary As incorporation into the crystal lattice of minerals) is characteristic for soil samples with geogenic load (VACHA et al. 2002). The increased arsenic distribution into more labile arsenic forms is typical for increased anthropogenic inputs. The labile arsenic forms are insignificant in both regional samples indicating marginal anthropogenic inputs of arsenic into the soils.

Arsenic concentration was assessed in the plants taken from 15 soil sample sites (Fig. 3). The highest concentration was observed in the plant samples from the less polluted soils confirming that the plants have taken arsenic primarily from the emission fallout and geochemically anomalous soils cannot be regarded risky for the plant production in the region. Higher arsenic concentration in plants can indicate the areas with the enhanced anthropogenic factors (traffic and urbanisation factors). The increased arsenic concentration in plants was observed in the local pollution sources – traffic lines (Fleky) and urban zones (surroundings of Sušice and Klatovy).

The enhanced arsenic concentration in the soil and parent rock materials can result in the surface and groundwater contamination. The spatial distribution of arsenic concentration in surface water was studied in the region (MAJER & VESELÝ 2005) and resembled the spatial distribution of arsenic concentration in soil (see Fig. 3). The anomalous arsenic concentrations in surface water were determined in the Volyně, Kašperské Hory, Hartmanice, and

Kvilda surroundings, or in the upper part of the Lipno reservoir. Considering the sediments taken from the streams less affected by the man, the arsenic concentration in sediments reflects the influence of the geological situation in this area confirming the geogenic origin of arsenic. The increased load of the surface water can indicate the groundwater pollution as well. NAKLADAL et al. (1997) surveyed the hydrogeological situation of the Kašperské Hory deposit and high arsenic concentration (0.305 mg .l⁻¹) was observed in the groundwater body in Kašperské Hory. The surface water was observed to be under influence of the hutch water below the Kašperské Hory deposit that caused arsenic enrichment of surface water (e.g., the Zlatý Potok stream) (NAKLADAL et al. 1997). The natural processes controlling arsenic solubility and mobility in solid–water system have been widely studied at the example of the Mokrsko gold deposit (DRAHOTA et al. 2009).

CONCLUSION

Various methods were used for the evaluation of arsenic occurrence in the soils of the Bohemian Forest region. The increased arsenic concentration in agricultural soils of the region was observed. Even if the relevant legal limit values for arsenic concentration in agricultural soils have been exceeded in many localities, arsenic load may not be regarded as risky due to prevailing geogenic source of arsenic content in the soils of the region. The arsenic concentration in plants from geochemically anomalous soils indicated that the arsenic load of geogenic origin could not be regarded risky for the agricultural production in the region. However, some risks can follow the arsenic occurrence concerning direct exposure, i.e., risks resulting from the inhalation, oral or dermal intake of arsenic in course of stay on the loaded soil. The enhanced arsenic concentration in the soil and parent rock materials can also contribute to surface water and groundwater contamination.

The results confirmed the geogenic source of arsenic load in soils of the region, however, the effect of anthropogenic factors can be observed in some parts of the region, especially in the connection with the historical gold mining activities or urbanization factors. Considering the samples taken from the areas less affected by the man, the arsenic concentration in soils reflects the geochemically anomalous substrate, so the influence of geological situation can be studied in this area. Zones of increased arsenic concentration resembled the geochemically anomalous substrate or the ore rich zones of gold bearing quartz veins. A high portion of arsenic is entrapped in forest soils around the historical gold mining working and thus land use management of these sites should allow for the arsenic occurrence in the soil. The soil condition changes, weathering and erosion fluxes of arsenic should be monitored in this area.

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