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RUDJER BOŠKOVIĆ INSTITUTE RADIOCARBON MEASUREMENTS VII

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Results of extensive and systematic radiocarbon dating of tufa samples and associated materials (wood, plants, moss, and peat) are presented in this paper. Samples were collected in Plitvice Lakes National Park, Central Croatia, Yugoslavia, where intensive precipitation of tufa has taken place over several geologic epochs in a typical Karst area. Problems associated with radiocarbon dating of tufa are discussed in a previous paper (Srdoč *et al,* 1980). The authors concluded that dating of tufa is feasible and reliable, at least in the specific case of Karst regions, where retention of groundwater is short. Tufa is precipitated as a result of decomposition of groundwater bicarbonates due to loss of CO_2, usually in waterfalls and cascades, and it is practically contemporaneous with living organic material. However, radiocarbon activity of modern tufa is lower than that of organic material due to dissolution of inactive carbonates (limestone) in groundwater. The initial activity of groundwater depends on the geology and vegetation of the area and it is widely discussed in the literature (Geyh, 1973). The initial activity, A_0, of tufa could be easily measured on recent samples, had not bomb-test contamination upset the equilibrium. Namely, while the atmospheric CO_2 and living matter responded relatively quickly to the injection of radiocarbon in the atmosphere, groundwater and, consequently, tufa showed a much slower and damped response. Therefore, we have based our estimation of the initial activity of tufa on measurements of samples of known age collected before the bomb-test era. An average value of the initial activity equal to 85% of modern has been obtained which is in accordance with data for groundwater activity in similar areas. Consequently, all radiocarbon ages of tufa samples in this paper are based on the Libby half-life of ^{14}C (5568 years) and *the initial radiocarbon activity equal to 85% of modern*. The modern standard is 0.95 of the activity of NBS oxalic acid. Errors quoted are based on counting statistics only and do not include uncertainties in ^{14}C half-life and in initial activity. The latter may introduce much larger errors, up to ± 1000 years, depending on the sampling site, as explained in the following sections. Whereas radiocarbon dating of Holocene tufa beds give reliable ages within the above specified errors, radiocarbon dating of old tufa beds is still questionable. Intrusion of minute quantities of modern calcareous material renders the ages of old (~30,000 yr) tufa useless. Research on measuring the age of old tufa deposits by other methods is in progress.

Preparation of wood, plant, and peat samples included pretreatment with boiling in 4% HCl and 4% NaOH. Tufa samples were mechanically cleaned by scraping off surface layers containing algae, moss, and/or lichens. Tufa, which contains up to 97% $CaCO_3$, was dissolved in diluted HCl and evolved CO_2 was frozen in a liquid N_2 trap. Subsequent counting, gas preparation, and purification is described in R, 1979, v 21, p 321-328, and the counting technique in R, 1971, v 13, p 135-140. Statistical processing of data has been computerized (Obelić and Planinić, 1977).

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GEOLOGIC, LIMNOLOGIC, AND BOTANICAL SAMPLES

1. Surface sampling

Most tufa samples were coll within Park area (44° 50′ N, 15° 35′ E) on surface of barriers, outcrops, and dry river beds without digging or drilling, except for Gavanovac series where existing cutting through tufa barrier was used to coll samples from depth of tufa bed.

Crna Rijeka series

A strong karstic spring feeds Crna Rijeka R. Tufa is not precipitated at the spring, which has fairly constant temperature throughout the year (8-10°C). Recent tufa is found ca 3km downstream where brook forms cascades. *Comment* (DS): lowest radiocarbon activity of groundwater and recent tufa in area.

Z-707. Teslin mlin waterfall 1 **63.9 ± 0.6% modern**

Recent tufa, surface layer deposited on moss, left bank of Crna Rijeka, 3km downstream from karst spring Crna Rijeka; coll Oct 1979. *Comment* (DS, NH): groundwater activity at spring C Rijeka: 59.7 ± 0.6% modern.

Z-752. Teslin mlin waterfall 2 **62.6 ± 0.6% modern**

Same as Z-707, right bank of Crna Rijeka.

Z-753. Teslin mlin waterfall 3 **64.0 ± 0.6% modern**

Same as Z-707; coll July 1980.

Bijela Rijeka series

Several small-capacity karst springs feed Bijela Rijeka R, which merges with Crna Rijeka R to form Matica R. *Comment* (DS): ^{14}C activity of Bijela Rijeka R and recent tufa are much higher than those of Crna Rijeka R, indicating different catchment area and/or hydrogeol of groundwater.

Z-754. Watermill 1 **85.3 ± 0.8% modern**

Tufa deposited on growing moss (*Cratoneurum commutatum*). Coll June 1980. *Comment* (DS, NH): Bijela Rijeka stream water activity: 75.7% modern; coll Nov 1979, same site.

74.6 ± 0.6% modern

Z-755. Watermill 2 **1050 ± 80**

Thick tufa deposits, presently ca 6m above stream level. Sample from top layer ca 0.5m below ground surface.

1.2 ± 0.3% modern

Z-684. Bijela Rijeka, dry tufa barrier **36,000 +2000 −1600**

Old tufa barrier 15m above present stream level, buried in alluvial deposits. NE flank opened during road construction. Deposition of tufa on moss can be easily recognized in structure of tufa beds.

Plitvički Ljeskovac series

Karst area at confluence of Crna Rijeka and Bijela Rijeka. Numerous old tufa barriers emerging from alluvial deposits as well as peat bogs are characteristic of landscape.

1.3 ± 0.3% modern

Z-809. Monument site 1 **36,000 +2200 −1800**

Old tufa barrier, partly recrystallized, 15 to 20m above and ca 70m from Matica R. Moss structure recognizable in non-crystalline parts of barrier. Crystallized structure covered by flowstone-like layers.

1.4 ± 0.3% modern

Z-936. Monument site 2 **34,500 +5100 −3200**

Old tufa barrier, block no. 3.

7.5 ± 0.3% modern

Z-811. Confluence site 1 **20,000 ± 500**

Dripstone or flowstone-like lining of tubing in solid tufa block. Tubes or channels were formed by decay of wood trunks or branches,

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structure of which is well-preserved. *Comment* (DS): calcareous linings are definitely younger than tufa matrix (see Z-809, -812) which forms huge blocks perforated by channels, indicating groundwater flow through old barrier. While old tufa morphology and abundance reflects paleoclimatic conditions similar to present climate, calcareous linings are amorphous and thin, indicating much colder climate and sparse vegetation. Thus, age of calcareous linings could be linked to interstadial thaw producing run-off and groundwater flow labeled by ^{14}C from thin vegetation layer consisting of algae, mosses, and lichens.

7.4 ± 0.3% modern
Z-685. Confluence site 2 **20,500 ± 500**

Calcareous lining similar to Z-811, same tufa barrier but different micro-location.

2.5 ± 0.3% modern
Z-812. Confluence site 3 **29,000 ± 1300**

Old tufa barrier, buried in alluvial deposits including terra rossa and calcareous sand. Sample taken on surface of outcrop, 10 to 15cm from holes lined with flowstone (Z-685, -811).

0.1 ± 0.3% modern
Z-918. Confluence site 4 **>37,000**

Old tufa barrier, block no. 2; sample taken 15 to 20cm laterally of natural drain hole (Z-685).

0.9 ± 0.3% modern
Z-919. Confluence site 5 **$37,000^{+6500}_{-3500}$**

Old tufa barrier, block no. 1; sample taken 10 to 15cm above natural drain hole (Z-811).

0.0 ± 0.3% modern
Z-813. Confluence site 6 **>37,000**

Outcrop of tufa in marshy field, often flooded during high water; sample taken 20 to 25m from old tufa barrier (Z-812).

1.5 ± 0.3% modern
Z-920. Tufa quarry **$33,500^{+1700}_{-1400}$**

Sample taken from old tufa quarry where tufa was cut for building. Quarry is inoperative since foundation of National Park.

0.7 ± 0.3% modern
Z-921. Vukmirović house **>37,000**

Tufa used for construction of walls, presumably from tufa quarry (Z-920). *Comment* (DS, NH): date confirms use of old tufa for building, although much younger Holocene tufa was found in other buildings in Park area.

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56.5 ± 0.5% modern
Z-700. Ex Bio-station **3350 ± 100**

Outcrops of tufa in marshy field; moss structure evident. Present flood area. *Comment* (DS): sample belongs to widespread group of Holocene tufa barriers. Both Holocene and pre-glacial tufas are found in same area, showing influence of geomorphol of karstic terrain on location of barriers; climatic conditions governed timing of growth of tufa.

Rječica series

Rječica Creek has no karst springs. Many woodland brooks form Rječica Creek. No recent tufa formations were found in woodland brooks. Recent tufa precipitation starts at first waterfall, although old Holocene tufa was found in Rječica stream bed upstream from present waterfall.

Z-748. Rječica waterfall 1 **86.4 ± 0.7% modern**

Recent tufa, surface layer deposited on moss (*Cratoneurum commutatum*). *Comment* (DS, NH): Rječica stream water activity: 87.7% modern; sample coll June 1980, same site.

78.7 ± 0.6% modern
Z-927. Rječica waterfall 2 **600 ± 100**

Small tufa barrier formed around waterfall, now above stream level. Date confirms recent tufa formation.

77.4 ± 0.6% modern
Z-750. Rječica waterfall 3 **750 ± 90**

Recent tufa in form of stump. Wood structure well-preserved.

81.0 ± 0.6% modern
Z-925. Rječica 1 **360 ± 100**

Thick tufa deposits, porous moss-like structure, Rječica tributary spring.

80.4 ± 0.6% modern
Z-924. Rječica 2 **430 ± 110**

Thick tufa deposit, porous and amorphous structure, adjacent to Z-925. *Comment* (DS): tufa structure reflecting deposition patterns does not influence radiocarbon content significantly (see also Z-922, -923).

80.2 ± 0.6% modern
Z-923. Rječica 3 **440 ± 90**

Inactive tufa barrier covered by humus and organic detritus. Typical porous moss-like structure (*Cratoneurum commutatum*).

80.0 ± 0.6% modern
Z-922. Rječica 4 **460 ± 90**

Porous, amorphous tufa from same barrier as Z-923.

78.6 ± 0.6% modern
Z-746. Rječica 5 **620 ± 70**

Porous, amorphous tufa from same deposit as Z-924; different micro-location. *Comment* (DS, NH): consistent with previous observations, ^{14}C tends to spread fairly uniformly throughout thick tufa deposits during formative period. Thus, average age of whole deposit is obtained rather than detailed stratigraphy.

66.0 ± 0.6% modern
Z-691. Rječica riverbed 1 **2050 ± 100**

Tufa from dry stream bed. Waterfall on Rječica R 1km downstream from bridge.

51.7 ± 0.5% modern
Z-926. Rječica riverbed 2 **4080 ± 110**

Tufa from stream bed, flooded at medium and high water.

40.1 ± 0.5% modern
Z-747. Rječica riverbed 3 **6200 ± 90**

Tufa from stream bed, flooded at high water. *Comment* (DS, NH): oldest Holocene sample. Repeated sampling at nearby site gave younger date (Z-926).

Cave Garden series

Cave Garden area covers 200m consisting of tufa barrier full of caves, galleries, and pits. Tufa barrier became partly inactive in historic times due to human interference with environment.

74.1 ± 0.3% modern
Z-663. Broken tufa stalactite **1100 ± 100**

Surface layer, flowstone structure.

73.8 ± 0.3% modern
Z-664. Broken tufa stalactite 2 **1150 ± 80**

Porous mossy structure, 25cm below surface.

74.8 ± 0.4% modern
Z-665. Broken tufa stalactite 3 **1030 ± 90**

Porous mossy structure, 53cm below surface.

74.4 ± 0.4% modern
Z-666. Broken tufa stalactite 4 **1070 ± 100**

Porous mossy structure, 83cm below surface. *Comment* (DS): data shows uniform distribution of ^{14}C in thick tufa column.

82.0 ± 0.3% modern
Z-824. Broken tufa column 1 **270 ± 100**

Base, surface layer, porous structure.

69.3 ± 0.3% modern
Z-911. Broken tufa column 2 **1650 ± 100**

Shaft, surface layer, flowstone structure.

Z-912. Broken tufa column 3 — **73.5 ± 0.3% modern** — **1170 ± 100**

Core at broken surface, 1.2m from edge.

Z-913. Broken tufa column 4 — **72.6 ± 0.3% modern** — **1270 ± 100**

Core at broken surface, 1m from edge. *Comment* (DS): data support theory of "tubular growth" of tufa under favorable conditions. Uppermost and outer layers are older than core. Tufa is deposited progressively on inner wall of duct until it becomes choked.

Z-821. Rock shelter 1 — **78.2 ± 0.6% modern** — **660 ± 90**

Sample from roof of rock shelter where tufa stalactite (Z-633 to -666) and column (Z-824 and -911 to -913) originated.

Z-823. Rock shelter 2 — **78.4 ± 0.6% modern** — **630 ± 100**

Sample from bottom of rock shelter; thick sediment filled with clastic material.

Z-909. Tufa cave 1 — **70.6 ± 0.6% modern** — **1500 ± 100**

Sample from bottom of small cave, 5m deep. Well-preserved imprints of leaves (*Fagus sylvatica*) found in sediments.

Z-910. Tufa cave 2 — **73.6 ± 0.6% modern** — **1160 ± 100**

Tufa column dividing cave, surface layer.

Z-953. Vertical wall 1 — **73.5 ± 0.6% modern** — **1160 ± 110**

Inactive tufa barrier, 12 to 15m high, vertical surface layer, 1.5m from bottom of barrier.

Z-955. Vertical wall 2 — **82.8 ± 0.7% modern** — **190 ± 100**

Fracture in tufa barrier, filled with dripstones.

Z-954. Cave garden — **77.0 ± 0.6% modern** — **785 ± 110**

Inactive tufa barrier in form of numerous caves, galleries, and channels. Sample from deepest cave. *Comment* (DS): radiocarbon activity of samples taken from bottom of tufa caves is not lower than that coll in open space, indicating simultaneous deposition of tufa throughout barrier during formative period of barrier growth.

Plitvica Creek series

Plitvica Creek forms waterfall, 86m high, at confluence of Korana R. No tufa forms at karst spring Izvor Plitvice. Although short, Plitvica Creek is interesting for study of tufa deposition. Starting with cold water and no tufa precipitation at spring, stream water gradually warms, forming thin tufa coating on moss and branches 2km downstream from spring.

Forming several cascades with thick tufa deposits right before waterfall, 86m high, Plitvica Creek ends in Korana R, 8 to 10°C warmer. Loss of CO_2 through aeration and decrease of $CaCO_3$ solubility due to warming of stream water are responsible for intensive tufa formation in Plitvica Waterfall area.

Z-805. Plitvica 1 **86.8 ± 0.7% modern**

Recent tufa deposited on moss growing on reef. *Comment* (DS, NH): Plitvica stream water activity: 85.2% modern, coll Oct 1980.

Z-701. Plitvica 2 **91.2 ± 0.7% modern**

Recent tufa deposited on moss (*Cratoneurum commutatum*) 2km downstream from Z-805 sampling site. *Comment* (DS, NH): higher activity agrees with observed downstream increase of radiocarbon content of stream and lake water (see Plitvice waters series).

41.7 ± 0.5% modern
Z-952. Plitvica 3 **5860 ± 130**

Dry bed of creek above Plitvica waterfall, 86m high.

75.9 ± 0.8% modern
Z-806. Plitvica 4 **900 ± 100**

Active tufa barrier at Hajduković Mill, surface layer, ca 10cm thick.

65.4 ± 0.6% modern
Z-706. Plitvica 5 **2140 ± 110**

Thick deposit of tufa adjacent to Plitvica waterfall.

59.2 ± 0.5% modern
Z-831. Hajduković Mill 1 **2960 ± 110**

Pit, 2 to 3m deep in flat terrace ("polje") near Hajduković Mill. Terrace is made entirely of tufa deposited by Plitvica R. Pits are result of collapsing of cave roof. Sample taken 80cm below ground surface.

61.0 ± 0.6% modern
Z-802. Hajduković Mill 2 **2710 ± 110**

Sample coll 80cm below ground on opposite side of same pit. Date confirms fairly uniform activity within layer.

55.6 ± 0.6% modern
Z-803. Hajduković Mill 3 **3480 ± 110**

Sample from ditch in tufa connecting pit and Plitvica creek.

45.0 ± 0.5% modern
Z-801. Hajduković Mill 4 **5230 ± 130**

Tufa from hollow wood trunk buried in thick tufa deposit, ca 2.5m below ground, 0.5m above bottom of pit.

48.8 ± 0.6% modern
Z-935. Hajduković Mill 5 **4550 ± 140**

Tufa surrounding hollow wood trunk in pit.

63.5 ± 0.6% modern

Z-800. Hajduković Mill 6 **3730 ± 110**

Wood from tree (conifer) buried in tufa, 2.5m below ground in pit. *Comment* (DS): age of wood and adjacent tufa agree fairly well if initial activity of tufa is taken equal to 0.7 of modern standard, which is reasonable value for Karst area. Better agreement cannot be expected because tufa did not grow on surface of tree; it was transported and deposited by floods.

Smolčića pećina cave series

Outcrop of old tufa, ca 60m above present level of Korana R, on steep right flank of gorge. Tufa deposits mark extinct tributary of Korana R.

0.5 ± 0.3% modern

Z-711. Smolčića pećina 1 **>37,000**

Tufa from bottom of horizontal cave, ca 12m deep, ca 60m above level of Korana R. Porous and amorphous structure.

2.9 ± 0.3% modern

Z-745. Smolčića pećina 2 **28,000 ± 900**

Tufa from bottom of cave, typical mossy structure.

1.5 ± 0.3% modern

Z-930. Smolčića pećina 3 **33,000 +5000 −3400**

Same as Z-745, from another micro-location within cave.

2.2 ± 0.3% modern

Z-742. Smolčića pećina 4 **30,000 ± 1700**

Tufa from entrance to cave.

8.0 ± 0.3% modern

Z-741. Smolčić plateau 1 **19,600 ± 300**

Outcrops of tufa emerging from soil in flat area right above cave roof. Tufa beds are probably inter-connected. Sample taken from surface of tufa block no. 1.

5.6 ± 0.3% modern

Z-744. Smolčić plateau 2 **22,400 ± 710**

Tufa, block no. 1, mossy structure, very hard.

3.9 ± 0.3% modern

Z-743. Smolčić plateau 3 **25,500 ± 1100**

Tufa, block no. 2, surface layer, very hard.

3.2 ± 0.3% modern

Z-934. Smolčić plateau 4 **27,100 ± 1300**

Tufa, block no. 1, surface layer removed, sample taken ca 10 to 15cm from surface. Due to tufa porosity, precipitation or surface water can easily penetrate thick tufa deposits.

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1.0 ± 0.3% modern

Z-933. Smolčić plateau 5 **$36{,}500^{+8600}_{-4000}$**

Tufa, block no. 3, very hard porous structure.

Lake Ciginovac series

Tufa samples with various morphologies were coll in cave above Lake Ciginovac. Measurement should reveal any difference in radiocarbon content caused by depositional patterns or influence of external contamination on tufa in variety of morphologic forms and structures. Samples of tufa in form of powder (Z-814), fine-grained compact sediment (Z-815), compact thick coating on limestone rock (Z-816), petrified moss (Z-817), and dripstone (Z-818) were measured. *Comment* (DS, NH): in most cases, powdered or structureless tufa is older than mossy structured tufa. Dripstone or flowstone layers are always youngest, which can be explained by subsequent formation of calcareous coating on tufa surface.

68.9 ± 0.6% modern

Z-814. Ciginovac 1 **1700 ± 110**

Powdered tufa coll from crevice in tufa barrier, NE shore of Lake Ciginovac.

69.7 ± 0.6% modern

Z-815. Ciginovac 2 **1610 ± 110**

Fine-grained compact tufa, same site as Z-814.

70.9 ± 0.6% modern

Z-816. Ciginovac 3 **1470 ± 100**

Tufa layer, 3cm thick, on bedrock, same site as Z-814.

72.4 ± 0.6% modern

Z-817. Ciginovac 4 **1300 ± 100**

Tufa in form of petrified moss (*Cratoneurum commutatum*); same site as Z-814.

74.9 ± 0.6% modern

Z-818. Ciginovac 5 **1020 ± 100**

Tufa covered by dripstone on surface. Outer layer containing mostly dripstone; same site as Z-814.

68.9 ± 0.6% modern

Z-820. Ciginovac plateau 1 **1700 ± 100**

Inactive tufa barrier above Lake Ciginovac, NE shore.

71.3 ± 0.6% modern

Z-904. Ciginovac plateau 2 **1420 ± 90**

Tufa sample, dripstone form, coll in crevice in tufa barrier.

72.1 ± 0.6% modern

Z-905. Ciginovac plateau 3 **1330 ± 100**

Tufa in form of petrified moss.

Upper Lakes

77.3 ± 0.6% modern
Z-956. Okrugljak 2100 ± 100

Active tufa barrier, right flank, presently dry. Hard mossy structure, covered with flowstone on surface.

63.5 ± 0.5% modern
Z-937. Galovac 2380 ± 100

Inactive tufa barrier near lake Galovac. Coll and subm by A Brnek, Natl Park Adm.

70.5 ± 0.6% modern
Z-917. Milino Jezero 1520 ± 80

Inactive tufa barrier 10m above and 50m from Milino Jezero pond.

56.5 ± 0.6% modern
Z-959. Pevalek Plaque 3340 ± 130

Zone of intensive tufa formation full of cascades, waterfalls, and streams. Sample coll from isolated tufa cliff, presently dry but surrounded by cascades and waterfalls. *Comment* (DS): date confirms that tufa formed over long period, presumably entire Holocene.

79.1 ± 0.5% modern
Z-958. Mali Prštavci 570 ± 100

Active tufa barrier, left flank. Sample coll in crevice close to waterfalls.

75.5 ± 0.6% modern
Z-957. Veliki Prštavci 2300 ± 110

Active tufa barrier, right flank. Sample coll in dry cave. Hard mossy structure.

Gradina series

Relatively isolated hill with remains of prehistoric ramparts ("gradina"). *Comment* (DS): outcrops of old tufa on top of hill puzzled early observers. Tufa barrier is autochthonous and belongs to old, preglacial formation. Thick tufa deposits at foothill are much younger Holocene features.

1.6 ± 0.3% modern
Z-667. Gradina, hilltop 1 33,000 $^{+2000}_{-1600}$

Remains of old tufa barrier, presently on top of Gradina hill, ca 30m above lake level.

2.1 ± 0.3% modern
Z-671. Gradina, hilltop 2 30,000 ± 1800

Same as Z-667, different micro-location.

2.1 ± 0.3% modern
+ 2000
Z-825. Gradina, hilltop 3 **31,000**
− 1600

Same as Z-667 except sample coll in small dry cave, protected from rain and snow.

0.4 ± 0.3% modern
Z-826. Gradina, hilltop 4 **>37,000**

Tufa powder coll from crevice in cave (see Z-825).

1.4 ± 0.3% modern
+ 2100
Z-827. Gradina, hilltop 5 **34,000**
− 1700

Outcrop of old tufa protruding through soil on top of Gradina hill. Hard, reddish tufa, mossy structure evident, contains iron oxide.

61.6 ± 0.6% modern
Z-900. Gradina, foothill 1 **2630 ± 110**

Thick deposits of tufa partly covered by soil and organic detritus. Compact but rather soft tufa.

65.1 ± 0.6% modern
Z-901. Gradina, foothill 2 **2170 ± 100**

Tufa deposits, 3 to 4m thick, forming caves, shelters, and galleries. Mossy structure well-preserved.

62.4 ± 0.6% modern
Z-902. Gradina, foothill 3 **2520 ± 110**

Same location as Z-901. Compact tufa, grained structure.

64.6 ± 0.6% modern
Z-903. Gradina, foothill 4 **2230 ± 100**

Same location as Z-901. Tufa, typical mossy structure (*Cratoneurum commutatum*).

Burget series

Two old tufa barriers, presently separated by lake water and recent tufa deposits. *Comment* (DS): contemporaneity of barriers helps construct contour lines of area in past.

62.6 ± 0.6% modern
Z-914. Burget 1 **2500 ± 110**

Old tufa barrier, submerged in Lake Burget, except crest. Hard, porous tufa sample coll from top of barrier.

63.8 ± 0.6% modern
Z-915. Burget 2 **2340 ± 120**

Old tufa barrier, above lake level.

76.6 ± 0.7% modern
Z-939. Burgetići **830 ± 110**

Active barrier above Lake Kozjak; soft porous tufa.

Z-674. Kozjak 1 **60.1 ± 0.7% modern**
2730 ± 100

Old tufa barrier, SW shore of Lake Kozjak, 15 to 20m above lake level. Original structure well-preserved. Sample coll from surface of tufa block.

Z-829. Kozjak 2 **63.2 ± 0.5% modern**
2420 ± 100

Same site as Z-674. Tufa sample coll in cave.

Gavanovac series

Cutting through tufa barrier was made during pathway construction in Park, near Lake Gavanovac. Cutting, 4m high and 1.6m wide, was suitable to coll samples from depth of tufa deposits, which would normally need drilling rig. Tufa samples ca $1dm^3$ in size were coll from vertical profile, starting at path level, in steps of 40cm up to 2.8m high. Uppermost sample is from crown of barrier at 4.05m. Two samples were coll 2m laterally from axis of vertical profile to check uniformity of ^{14}C distribution in horizontal layer. Five samples were coll in horizontal profile at 1.6m above path level. Starting with surface layer, 5cm thick, sampling proceeded at 10cm steps up to 45cm. *Comment* (DS): no distinct gradient was found in any direction, except in horizontal profile, where small but systematic decrease of ^{14}C activity was detected. This is consistent with measurements of tufa samples from other sites (see Cave Garden series, above). ^{14}C tends to spread uniformly in tufa deposits during build-up process, obliterating much stratigraphy. ^{14}C age gives average of all tufa deposits. In most cases, build-up period is much shorter than age of tufa beds, which diminishes inherent error in ^{14}C dating of tufa.

Vertical profile

Z-620. G-1 **57.5 ± 0.5% modern**
3200 ± 90

Cutting through dry tufa barrier; height (H) = 0m, depth (D) = 10cm.

Z-621. G-2 **58.9 ± 0.6% modern**
3000 ± 100

H = 0.4m, D = 10cm.

Z-622. G-3 **58.2 ± 0.6% modern**
3100 ± 110

H = 0.8m, D = 10cm.

Z-662. G-4 **59.1 ± 0.6% modern**
2980 ± 110

Lateral sampling; H = 0.8m, D = 20cm, 2m right from vertical profile.

Z-623. G-5 **62.6 ± 0.6% modern**
2500 ± 80

Vertical profile; H = 1.2m, D = 10cm.

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Z-661. G-6 **58.5 ± 0.6% modern**
3060 ± 110

Lateral sampling; H = 1.2m, D = 20cm, 2m left from vertical profile.

Z-624. G-7 **60.4 ± 0.6% modern**
2800 ± 100

Vertical profile; H = 1.2m, D = 20cm.

Z-628. G-8 **62.8 ± 0.3% modern**
2480 ± 100

H = 2m, D = 20cm.

Z-633. G-9 **63.0 ± 0.3% modern**
2450 ± 110

Vertical profile, wood-shaped tufa; H = 2.3m; original structure of tree trunks and branches well-preserved.

Z-630. G-10 **60.6 ± 0.6% modern**
2770 ± 100

H = 2.4m, D = 20cm.

Z-644. G-11 **62.1 ± 0.6% modern**
2570 ± 110

H = 2.6m, D = 20cm.

Z-631. G-12 **61.5 ± 0.6% modern**
2640 ± 110

H = 2.8m, D = 20cm.

Z-632. G-13 **61.6 ± 0.6% modern**
2630 ± 110

Vertical profile, top of barrier; H = 4.05m, D = 20cm.

Horizontal profile

Z-625. G-14 **62.0 ± 0.6% modern**
2580 ± 110

Horizontal profile; H = 1.6m, surface layer, 5cm thick.

Z-626. G-15 **61.0 ± 0.6% modern**
2720 ± 100

H = 1.6m, D = 10cm.

Z-660. G-16 **59.8 ± 0.6% modern**
2880 ± 100

H = 1.6m, D = 20cm.

Z-681. G-17 **59.6 ± 0.5% modern**
2910 ± 110

H = 1.6m, D = 30cm.

Z-682. G-18 **58.7 ± 0.6% modern**
3030 ± 110

H = 1.6m, D = 40cm.

Korana River series

Last thick deposits of tufa, N boundary of Natl Park. Tufa precipitation rate diminishes as Korana R slows down. *Comment* (DS, NH): high ^{14}C activity of freshwater and recent tufa.

Z-704. Korana 1 **90.9 ± 0.7% modern**

Recent tufa deposited on moss covering river bed. *Comment* (DS, NH): Korana R water activity: 93.1% modern.

73.0 ± 0.6% modern
Z-686. Korana 2 **1230 ± 100**

Cutting through thick deposit of tufa, 6 to 7m above Korana R. Fine-grained structure.

Milka Trnina Waterfalls series

Area of copious tufa deposition.

Z-658. MT-1 **91.3 ± 0.8% modern**

Recent tufa deposited on moss growing on cliffs. Moss (*Cratoneurum commutatum*) is continually splashed or sprayed by lake water.

Z-659. MT-2 **90.0 ± 0.7% modern**

Soft tufa layer, 3 to 4cm thick, deposited under growing moss. Moss roots and organic detritus removed.

2. *Underwater sampling*

Bathymetric measurements revealed underwater tufa barriers in several lakes. Downstream growth of new tufa barriers caused flooding and inactivation of upstream barriers which are now several meters below present lake surface. Samples coll 1980 by Pragoaquanaut scuba divers, Prague, ČSSR, led by J Svetly.

Lake Gradinsko Jezero series

Sample of tufa coll from surface of submerged tufa barrier.

72.8 ± 0.6% modern
Z-832. Lake Gradinsko Jezero 1 **1250 ± 100**

Underwater tufa barrier; grained structure covered with algae; depth: 5.5m. Algae, roots, and mud removed.

70.3 ± 0.6% modern
Z-833. Lake Gradinsko Jezero 2 **1540 ± 100**

Same as Z-832 but different micro-location.

74.2 ± 0.6% modern
Z-834. Lake Gradinsko Jezero 3 **1090 ± 110**

Same as Z-832; depth: 3m.

Lake Kozjak series

Samples of tufa coll from surface of submerged tufa barrier.

72.6 ± 0.6% modern

Z-843. Lake Kozjak 1 **1270 ± 100**

Underwater tufa barrier, spongy structure on surface. SW flank of barrier; depth: 5.5m.

71.4 ± 0.6% modern

Z-842. Lake Kozjak 2 **1420 ± 110**

Same as Z-843, NE flank of barrier.

72.4 ± 0.6% modern

Z-838. Lake Kozjak 3 **1290 ± 100**

Central sec of underwater tufa barrier. Spongy or "cauliflower" structure, filled with lake sediment in pores. Mud and surface layer of algae removed; depth: 7m.

75.3 ± 0.6% modern

Z-840. Lake Kozjak 4 **970 ± 100**

Same as Z-838; depth: 12m.

75.3 ± 0.6% modern

Z-841. Lake Kozjak 5 **980 ± 100**

Same as Z-838; depth: 15m.

3. Pre-bomb-test samples of wood, moss, and tufa

Pevalek collection series

^{14}C activity of recent tufa has not followed sharp increase of ^{14}C activity in biosphere caused by nuclear weapon tests. Increased activity of groundwater, tufa, and aquatic plants due to increased activity of atmospheric CO_2 in past decades can be obtained by comparison of activity of recent material with that from pre-bomb-test era, providing that age of latter is known. We found several such samples of wood encrusted with tufa and moss with tufa substratum from colln of late academician Ivo Pevalek. *Comment* (DS): measurements of samples coll in 1937 and comparison with recent data leads to two important conclusions: 1) activity of recent tufa is comparable to activity of "pre-war" tufa (ca 1937). Depending on sampling site, activity of recent tufa varies from 85% to 91% modern, whereas activity of "pre-war" tufa varies from 71% to 88% modern. Range of activities of recent tufa was measured on 10 samples; "pre-war" tufa was measured on 2 samples only, 2) use of average initial activity of 85% modern may introduce error up to 1000 yr. However, low activity equal to 70% modern is found in limited region close to karst springs; largest part of tufa deposits is in lake area where ^{14}C activity is fairly uniformly distributed ca 85% modern. Thus, estimated error is ± 500 yr for most samples.

Z-847. Wood coated with tufa **98.1 ± 0.7% modern**

Wooden branch (*Fagus sylvatica*), 4cm diam, coated with tufa layer, 2 to 3cm thick. Coll 1937 by I Pevalek and stored in dry cabinet. Subm by A Brnek, Natl Park Admin. Micro-location not known. *Comment* (DS): Suess effect is evident even though entire area is not industrialized.

Prevailing westerly winds could account for depleted ^{14}C activity between two World Wars.

Z-848. Tufa coating on wood **88.5 ± 0.7% modern**

Tufa coating, 2 to 3cm thick, on wood surface (sample Z-847). Tufa was scraped off and dissolved in HCl. *Comment* (DS): ratio of practically contemporaneous pre-bomb-test wood and tufa ^{14}C activities: $A_0 = 0.9$. This value is higher than $A_0 = 0.85$, which is used in this paper as average value. Higher and lower values of A_0 were also found, depending on sampling site location (see Z-857 and -855).

Z-853. Plant stalks **92.9 ± 0.8% modern**

Woody stalks (unid. sp), plant stalks, moss, and tufa from sample stored in cabinet. Coll by I Pevalek, ca 1937. *Comment* (DS): low ^{14}C content of relatively recent plants indicates absorption of CO_2 depleted in ^{14}C from decomposition of hydrocarbonates.

Z-855. Tufa substratum **68.8 ± 0.6% modern**

Surface layer, 3cm thick, soft crumbly structure with moss roots. Roots and other organic material removed.

Z-856. Tufa substratum **69.6 ± 0.8% modern**

Lower layer, 3cm below surface, 3cm thick, soft crumbly structure.

Z-857. Moss **72.8 ± 0.7% modern**

Cratoneurum commutatum, grown on tufa, coll ca 1937 by I Pevalek; stored in dry condition in cabinet together with tufa substratum. Tufa removed mechanically and measured separately (see Z-855 and -856). Moss treated with HCl to remove remaining carbonates.

Z-908. Wooden post **96.5 ± 0.7% modern**

Wooden post covered with tufa layer, 2 to 3cm thick. *Comment* (DS): sample contains mostly sapwood and bark. Post was used to support small bridge on Labudovac plateau and was replaced. No record of this exists but ^{14}C activity of sapwood clearly show that wood was cut before bomb-test contamination.

Z-907. Tufa coating on wooden post **81.6 ± 0.7% modern**

Tufa coating, 2 to 3cm thick, on wooden post (Z-908). *Comment* (DS): ratio between tufa and adjacent wood activities: $A_0 = 0.845$.

4. Botanical samples, Plitvice Park area

Z-668. Terrestrial plant 1 **134.5 ± 1.1% modern**

Dry leaves (*Fagus sylvatica*) coll Nov 1976, Lake Kozjak area.

Z-656. Terrestrial plant 2 **130.4 ± 1.0% modern**

Twigs (*Salix cinerea*) coll March 1978, M Trnina Waterfalls. Plant roots submerged in lake water. *Comment* (DS): lake water activity: 85% modern; atmospheric CO_2 activity: 131.5% modern (March 1978).

Z-657. Moss 1 **91.7 ± 1.0% modern**

Moss (*Cratoneurum commutatum*) coll March 1978, M Trnina Waterfalls. Moss growing on tufa substratum, constantly splashed with water.

Z-679. Moss 2 **82.4 ± 0.7% modern**

Moss (*Cratoneurum commutatum*) growing on tufa substratum, constantly submerged in lake water, Galovac cascades.

Z-678. Moss 3 **83.0 ± 0.7% modern**

Moss (*Cratoneurum commutatum*) growing on tufa substratum, presently dry, Galovac cascades area. *Comment* (DS): although exposed to atmospheric CO_2, activity of which was 131.5%, moss activity is much closer to lake water or recent tufa activity.

Z-677. Aquatic plant **77.4 ± 1.0% modern**

Aquatic plant (*Potamogetum perfoliatus*) coll Spring 1978, Lake Galovac.

89.5 ± 0.7% modern
Z-846. Submerged wood 1 **800 ± 90**

Tree (*Abies sp* L) emerging from Lake Kozjak bottom in upright position; depth: 9m, height: 7.5m. Sample taken from core of trunk.

91.5 ± 0.8% modern
Z-845. Submerged wood 2 **710 ± 90**

Same as Z-846, outer layer of tree trunk. *Comment* (DS): rate of growth of tufa barrier crest can be calculated on assumption that tree was killed by flooding. Based on age of outer layer and depth, average growth rate of 1.3cm/yr is obtained. This agrees well with observations on recent rise of lake level.

5. Surface water activity

Z-692. Crna Rijeka spring **59.7 ± 0.6% modern**

Karst spring, main water resource of area. Temperature fairly constant, averaging 7.8°C. Tritium activity close to mean yearly activity of precipitation. Sample coll Oct 1979.

Z-694. Bijela Rijeka spring **75.7 ± 0.7% modern**

Several karst springs feed Bijela Rijeka R. Sample coll Oct 1979 ca 300m downstream from spring. *Comment* (DS, NH): abundant vegetation along stream increases ^{14}C activity which is probably lower at spring.

Z-942. Prošće **78.7 ± 0.7% modern**

Lake water, W shore of Prošćansko Jezero, coll Oct 1981.

Z-708. Plitvica **85.3 ± 0.7% modern**

Stream water, tapped from karst spring, coll Oct 1979.

Z-710. Rječica **88.8 ± 0.7% modern**

Stream water, coll Oct 1979. Rječica brook has no karst spring.

Z-672. Lake Kozjak 1 **84.5 ± 0.7% modern**

Lake water from NW shore, coll April 1979.

Z-693. Lake Kozjak 2 **89.3 ± 0.7% modern**

Lake water coll at outlet Oct 1979. Temperature of lake water is 8 to 10°C above karst spring temperature in summer.

Z-709. Korana River **92.1 ± 0.8% modern**

River water coll Oct 1979 under bridge on Karlovac-Plitvička Jezera hwy. Intensive tufa precipitation ends at this point.

6. Peat samples

Plitvički Ljeskovac peat bog series

Peat bog near Plitvički Ljeskovac, Plitvice Lakes Natl Park. Luličina Bara peat bog is in area of intensive tufa precipitation. Peat samples were extracted with Dachnowsky-type hand-corer by A Šercelj for pollen analysis (Culiberg and Šercelj, 1981).

Samples were treated with 4% HCl and 4% NaOH at 80°C, thoroughly washed and dried. Depth is given in cm below bog surface. *Comment* (DS): coincident beginning of tufa and peat formation in Holocene at ca 6200 ± 200 yr BP may be explained by possibility that tufa formation and intensive vegetation started simultaneously when climatic conditions at this alt (640m) became favorable for both processes.

Z-636.	**5-30cm**	**190 ± 100**
Z-637.	**30-60cm**	**1050 ± 70**
Z-640.	**60-90cm**	**1240 ± 90**
Z-641.	**90-120cm**	**1670 ± 70**
Z-642.	**120-150cm**	**1860 ± 90**
Z-643.	**150-180cm**	**2060 ± 100**
Z-638.	**180-210cm**	**2380 ± 80**
Z-946.	**300-320cm**	**2830 ± 110**
Z-947.	**400-420cm**	**3030 ± 110**
Z-969.	**440-460cm**	**3140 ± 110**
Z-960.	**460-480cm**	**3520 ± 110**
Z-970.	**540-560cm**	**3810 ± 110**
Z-949.	**600-620cm**	**3950 ± 110**
Z-950.	**680-700cm**	**4580 ± 120**
Z-972.	**740-760cm**	**5160 ± 130**
Z-961.	**840-860cm**	**5530 ± 130**

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