

Using Dye-Tracing and Chemical Analyses to Determine Effects of a Wastewater Discharge to Jam Up Creek on Water Quality of Big Spring, Southeastern Missouri, 2001

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Introduction

On July 5, 2001, approximately 50,000 gallons of partially treated wastewater was accidentally discharged from the Mountain View wastewater-treatment plant in Howell County, Missouri, into nearby Jam Up Creek. The creek is a tributary of the Jacks Fork, a recreational stream administered by the National Park Service (NPS) as part of the Ozark National Scenic Riverways in southeastern Missouri (fig. 1). Jam Up Creek is located in a mature karst terrain and normally loses all surface flow about 0.5 to 1.0 river mile downstream from the wastewater-treatment plant. Historical dye-trace investigations conducted in 1972 (Aley, 1975) and 1982 [unpublished data on file at the Missouri Department of Natural Resources, Geological Survey and Resources Assessment

Division (MDNR-GSRAD)] indicate the existence of a subsurface hydraulic connection between the losing reach of Jam Up Creek and Big Spring on the Current River in the Ozark National Scenic Riverways (fig. 1; Imes and Kleeschulte, 1995). The time for dye to

travel in the ground-water flow system through the karst terrain from Jam Up Creek to Big Spring (a distance of 38 miles) was estimated to be 35 to 40 days, which means that water transported the dye at a rate of about 0.95 to 1.1 mi/d (mile per day). The quantity

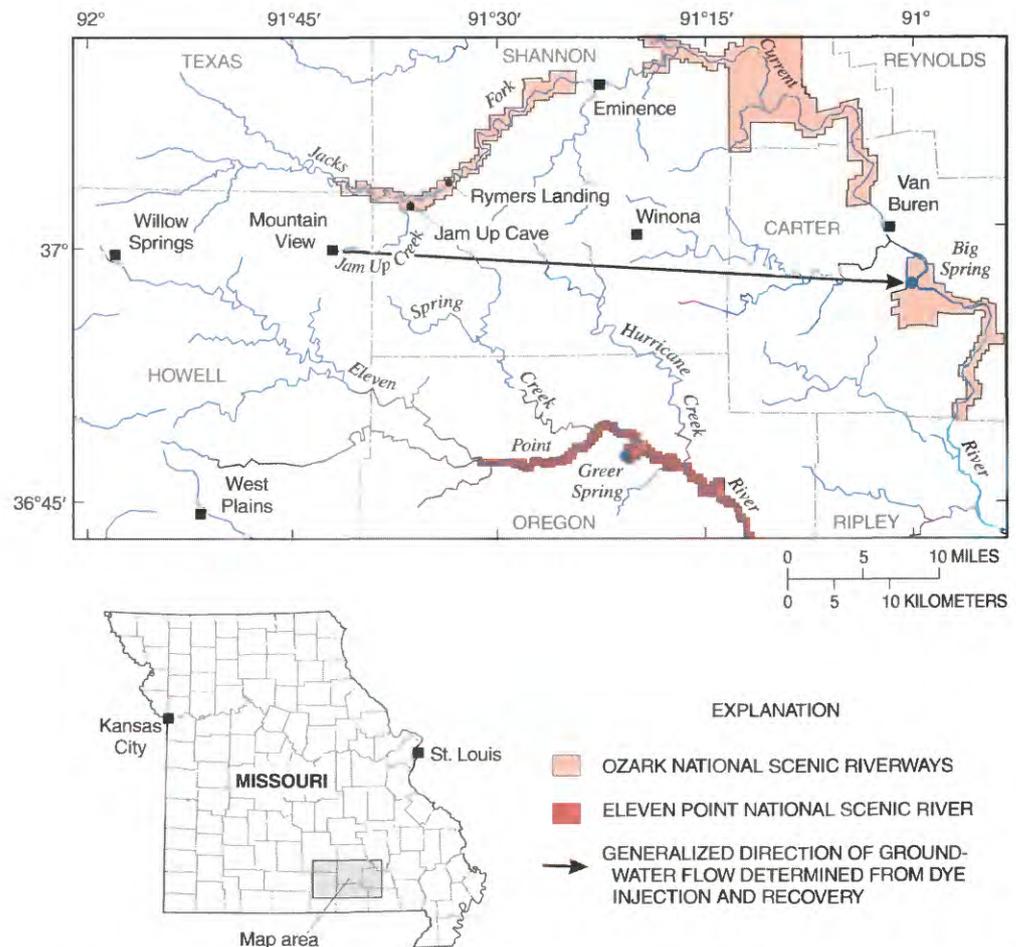


Figure 1. Location of Rhodamine-WT dye injection into Jam Up Creek at Mountain View, Missouri, on July 10, 2001, and monitored potential dye recovery sites.



of wastewater discharged at the wastewater-treatment plant and the known hydraulic connection between Jam Up Creek and Big Spring caused concern at the NPS about possible effects on water quality of Big Spring. Discharge from Big Spring could affect water quality of the Ozark National Scenic Riverways. This report describes results of a study conducted by the NPS and the U.S. Geological Survey (USGS) to refine the time of travel for ground-water flow through the karst terrain from Jam Up Creek to Big Spring and to determine the possible effects on water quality in Big Spring caused by the wastewater discharged to Jam Up Creek.

Dye Injection at Jam Up Creek and Recovery Procedures

Rhodamine-WT dye [4.5 lb (pounds)] was injected on July 10, 2001, into Jam Up Creek (lat-

itude 36°59'52" and longitude 91°40'22") about 1,200 ft (feet) downstream from the Mountain View wastewater-treatment plant by pouring dye directly into the small flow that was present in the creek channel. The estimated discharge of Jam Up Creek at the injection site was 0.5 ft³/s [cubic foot per second; 224 gal/min (gallons per minute)]. The flow of Jam Up Creek was zero 1 mile downstream from the injection site and several large pools were observed along this 1-mile losing reach, a common occurrence in losing streams in the Ozarks.

Water samples were collected by the NPS from Jam Up Creek at Jam Up Cave (latitude 37°02'19" and longitude 91°36'20"), Jacks Fork at the mouth of Jam Up Creek (latitude 37°02'26" and longitude 91°36'15"), and Jacks Fork at Rymers Landing (latitude 37°03'36" and longitude 91°33'48") and analyzed for the presence of Rhodamine-WT dye.

These sites are 7.5, 7.6, and 11.2 river miles downstream from the wastewater-treatment plant. Water samples were collected by the USGS from Big Spring using an automatic sampler programmed to collect one sample every 12 hours from July 21 to September 21, 2001. Dye concentrations in water from Big Spring peaked on August 21 during this time period (fig. 2). After September 21 the sampler was reprogrammed to collect one sample every 24 hours to investigate the possibility that a secondary dye pulse might occur as the spring conduit system was flushed during storms following the dye injection. No secondary pulse was detected.

Concurrent with the USGS investigation, the MDNR-GSRAD was investigating the possibility that wastewater was contaminating water in domestic wells in the vicinity of the wastewater-treatment plant. Water samples were collected by the Missouri Department of Health (MDOH) and MDNR-GSRAD from 54 domestic wells on August 30 and tested for the presence of Rhodamine-WT dye. Dye was detected in a sample from one domestic well located about 1.7 miles east of the wastewater-treatment plant and 1.5 miles east of the dye-injection site. Results of the 1982 dye trace and the 2001 domestic well study are on file at the MDNR-GSRAD offices in Rolla, Missouri (Peter Price, Missouri Department of Natural Resources, Geological Survey

and Resources Assessment Division, written commun., 2002).

Dye-Detection Methods

Water samples were analyzed for the presence of dye using a scanning spectrofluorophotometer. A scanning spectrofluorophotometer detects dye by passing a range of wavelengths of light through a sample and measuring the fluorescent emission light intensity as a function of the emission wavelength of light from the sample. The analysis is presented as a graph of emission light intensity versus emission light wavelength. If Rhodamine-WT dye is present in the sample, the graph will exhibit an intensity peak at about 576 nm (nanometer) wavelength.

Activated charcoal has the ability to adsorb large quantities of dye on its surface. Packets of activated charcoal were placed in Jam Up Creek at Jam Up Cave, Jacks Fork at Rymers Landing, and Big Spring to provide a second method of recovering the injected dye. The packets were replaced at approximately 1- to 2-week intervals and were then analyzed for the presence of dye. The analysis included drying the exposed charcoal for 24 hours, immersing the dry charcoal in a solution of 90 percent isopropyl alcohol and 10 percent fuming ammonium hydroxide for 4 to 6 hours to dissolve the absorbed dye, and analyzing the solution for dissolved dye using a scanning spectrofluorophotometer.

Activated charcoal tends to concentrate other fluorescent chemical compounds that may be present in the water as well as dye used in a tracing test; consequently, the exposed charcoal may exhibit a large background fluorescence that can mask the fluorescent signature of the injected dye.

Detection of Dye at Monitored Sites

The injected Rhodamine-WT dye was detected in water samples (fig. 2) and charcoal packets from Big Spring. No dye was detected in water samples and charcoal packets from Jam Up Creek at Jam Up Cave, Jacks Fork near the mouth of Jam Up Creek, or Jacks Fork at Rymers Landing. These results verified the subsurface hydraulic connection between Jam Up Creek and Big Spring, and indicated that none of the lost flow from Jam Up

Creek resurfaces into Jam Up Creek downstream from the 1-mile losing reach. Dye was detected in water samples from Big Spring from about August 12 until about September 20 with the peak Rhodamine-WT fluorescence intensity occurring on August 21 (fig. 3). At the fluorescence peak, the dye had traveled a distance of 38 miles in 42 days corresponding to an average flow rate of 0.9 mi/d. No secondary dye peak was detected in water samples collected from Big Spring from October 2, 2001, to January 31, 2002.

Quantification of Recovered Dye at Big Spring

Several factors can hinder the transport of dye from the injection point to the recovery point. These factors include entrapment of the dye in subsurface cavities where ground-water

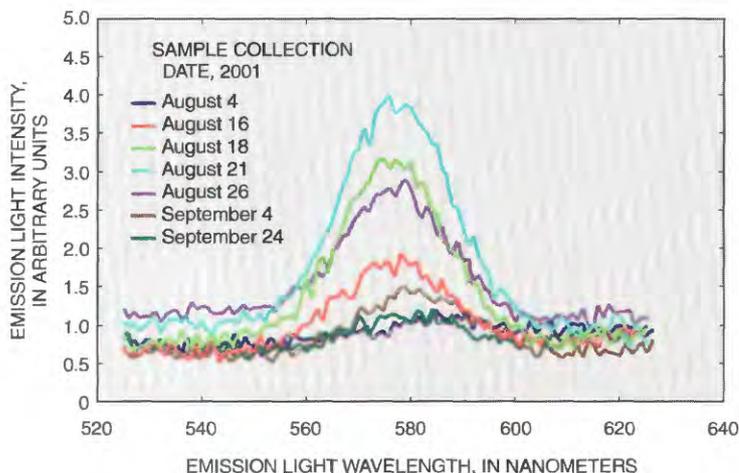


Figure 2. Emission spectra of water samples from Big Spring from 520 nanometer to 640 nanometer wavelength showing increase and subsequent decrease of Rhodamine-WT dye concentration at the spring.

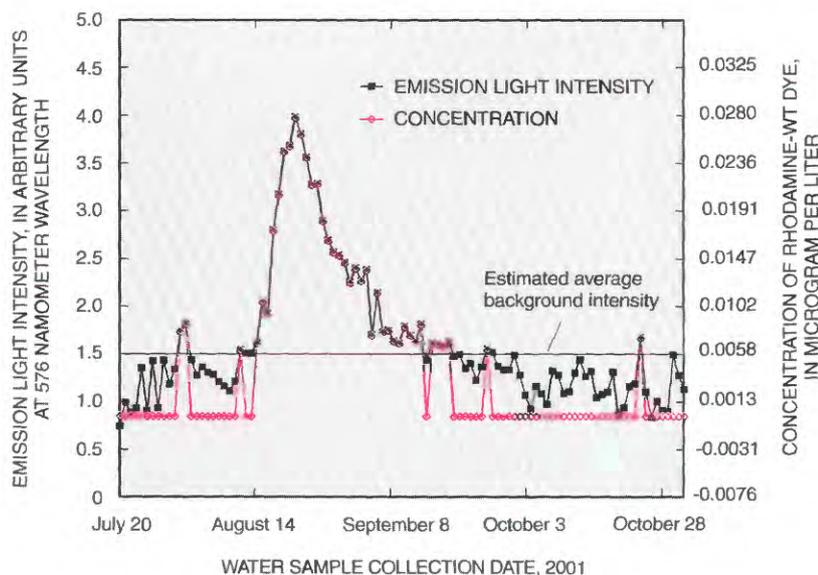


Figure 3. Emission light intensity of Rhodamine-WT dye at 576 nanometer wavelength and concentration of Rhodamine-WT in water samples from Big Spring collected from July 20 to October 31, 2001.

flow velocities are small, chemical and biological degradation of the dye, and adsorption of the dye on clay and rock surfaces. Even successful dye-trace investigations are rarely, if ever, characterized by recovery of 100 percent of the injected dye. The amount of recovered Rhodamine-WT dye at Big Spring was determined by converting the measured emission light intensity of water samples from Big Spring at 576 nm to dye concentrations, determining the daily dye load as the product of dye concentration and daily mean spring discharge, and summing the dye load across the time interval during which Rhodamine-WT dye was detected at Big Spring. Regression analysis was used to develop a correlation between the 576 nm emission light intensity measured by the scanning spectrofluorophotometer and known concentrations of dye standards.

Rhodamine-WT dye standards were prepared by diluting highly concentrated dye (as purchased from the manufacturer) to concentrations of 0.010, 0.015, 0.020, 0.030, and 0.040 $\mu\text{g/L}$ (microgram per liter). The stan-

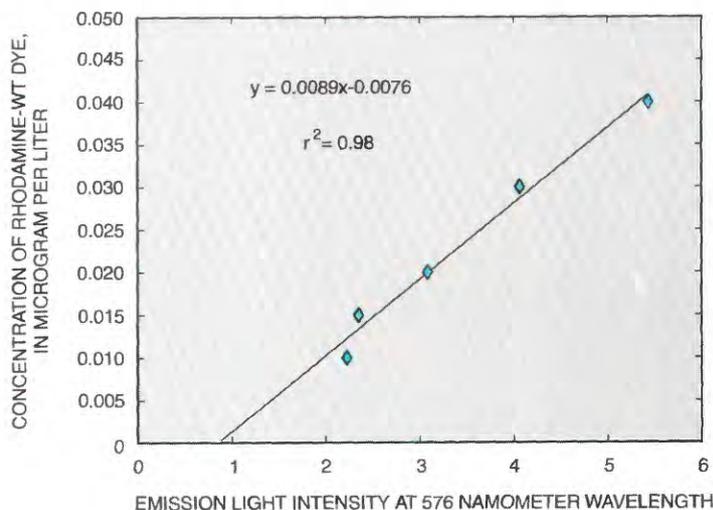


Figure 4. Calibration of scanning spectrofluorophotometer emission light intensity for Rhodamine-WT dye (576 nanometer wavelength) to prepared standards of known dye concentrations in water.

dards were analyzed using the same methods used to analyze water samples collected in the field. The concentration of the standards had a linear relation to emission light intensity as described by equation 1:

$$y = 0.0089x - 0.0076, \quad (1)$$

where y is dye concentration and x is emission light intensity (fig. 4). The calculated concentration of Rhodamine-WT dye in Big Spring water samples ranged from 0.006 to 0.0278 $\mu\text{g/L}$ (fig. 3). Calculated concentrations less than 0.006 $\mu\text{g/L}$ were assumed to be zero for the purpose of determining dye loads, because this concentration corresponded to the estimated average background of 1.5 emission light intensity at 576 nm for the water samples (fig. 3).

Ground-water discharge at Big Spring during the dye-trace investigation ranged from a low

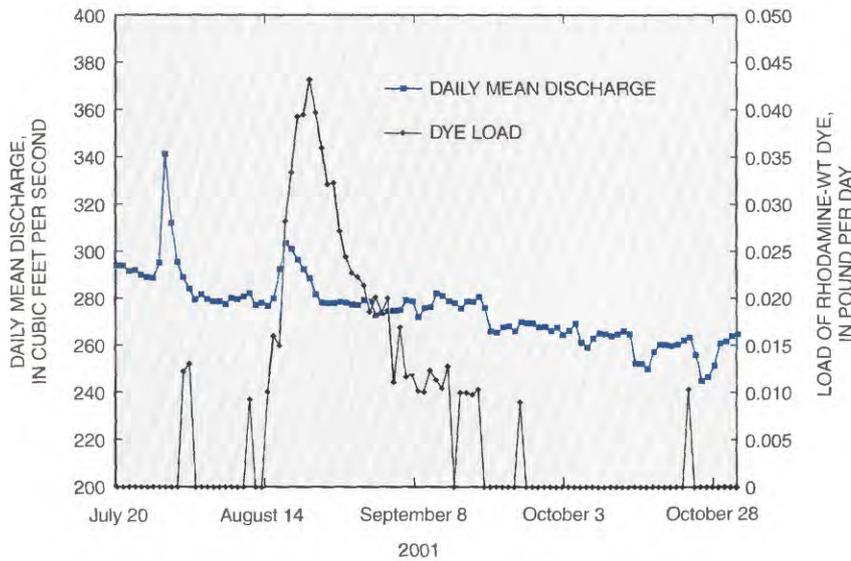


Figure 5. Daily mean discharge of Big Spring and estimated daily load of Rhodamine-WT dye in water discharging from Big Spring.

flow of 244 ft³/s to a high flow of 342 ft³/s (fig. 5). Rainfall during the summer caused the spring discharge to peak at 342 ft³/s on July 28 and at 303 ft³/s on August 17. The maximum dye load in the spring water occurred on August 21, at 0.043 lb/d (pound per day; fig. 5). An estimated 0.77 lb, or 17 percent, of the 4.5 lb of dye injected into Jam Up Creek was discharged from the ground-water flow system through Big Spring.

Effect of Wastewater on Water Quality at Big Spring

To determine the effect of the partially treated wastewater on water quality at Big Spring, one sample of contaminated water from Jam Up Creek and two samples of water from Big Spring

were analyzed for a suite of 67 compounds commonly associated with wastewater. The Jam Up Creek sample was collected on July 12, approximately 1,200 ft downstream from the wastewater-treatment plant, 7 days after the wastewater discharge into Jam Up Creek. The sample contained 35 of the 67 compounds (table 1). Compounds detected in higher concentrations include 3-beta-coprostanol (a compound found in human and carnivorous animal feces), beta-sitosterol (a common sterol found in plants and oils extracted from plants), caffeine (a compound found in tea and coffee), cholesterol (the principal sterol found in human and animal body tissues and fats), N,N-diethyltoluamide (used in insect repellents), NPEO2-total (used as a surfactant in detergents), and para-nonylphenol-total (used as a surfactant in detergents).

A water sample collected from Big Spring on July 10, 2001, before the wastewater could travel to the spring, contained none of the 67 wastewater compounds. A sample of water collected from Big Spring on August 17, 4 days before the peak dye concentrations were measured in the spring water, contained phenol and cholesterol (table 1). The detection of these two wastewater compounds in the spring sample does not necessarily indicate contamination from the wastewater discharged into Jam Up Creek. Phenol is a compound commonly used in disinfectants for toilets and cesspools (a public toilet is located near Big Spring) and is present in the manufacture of some dyes, and cholesterol is present in animal waste.

The daily mean discharge of Big Spring on August 17, 2001, was 303 ft³/s (fig. 5). At this flow rate, Big Spring discharges about 196 million gallons a day, which is a volume of water 3,900 times larger than the 50,000 gallons of wastewater that discharged into Jam Up Creek. Thus, the wastewater that entered the ground-water flow system at Mountain View through the losing reach of Jam Up Creek was substantially diluted by the time it discharged at Big Spring. The wastewater compounds detected in Jam Up Creek may have been present in the water discharging at Big Spring at concentrations well below laboratory reporting limits.

Table 1. Results of laboratory analyses of water samples collected from Jam Up Creek and Big Spring in July and August 2001, for chemical compounds commonly associated with wastewater

[Shading indicates detected compound; e, estimated; <, less than; µg/L, micrograms per liter; AHTN, acetyl hexamethyl tetrahydronaphthalene; BHA, 3-tert-Butyl-4-hydroxy anisole; HHCB, hexahydrohexamethylcyclopentabenzopyran; NPEO2, nonylphenol diethoxylate; OPEO1, octylphenol monoethoxylate; OPEO2, octylphenol diethoxylate]

Compound	Jam Up Creek July 12 µg/L	Big Spring Aug 17 µg/L	Minimum reporting limit µg/L	Compound	Jam Up Creek July 12 µg/L	Big Spring Aug 17 µg/L	Minimum reporting limit µg/L
1,4-Dichlorobenzene	e 0.160	<0.500	0.5	Esterone	e 2.100	<5.000	5
1-Methylnaphthalene	< .500	< .500	.5	Ethanol,2-butoxy-,phosphate	5	< .500	.5
2,6-Dimethylnaphthalene	< .500	< .500	.5	Ethyl citrate	e .360	< .500	.5
2-Methylnaphthalene	< .500	< .500	.5	Fluoranthene	< .500	< .500	.5
3-beta-Coprostanol	7.4	<2.000	2	HHCB	e .180	< .500	.5
4-Cumylphenol	<1.000	<1.000	1	Indole	1	< .500	.5
4-n-Octylphenol	e .430	<1.000	1	Isoborneol	< .500	< .500	.5
4-tert-Octylphenol	e .970	<1.000	1	Isophorone	< .500	< .500	.5
5-Methyl-1H-benzotriazole	<2.000	<2.000	2	Isoquinoline	< .500	< .500	.5
17-alpha-Ethynyl esterdiol	e .073	<5.000	5	Menthol	.5	< .500	.5
17-beta-Estradiol	e .089	<5.000	5	Metalaxyl	< .500	< .500	.5
Acetophenone	e .300	< .500	.5	Methyl salicylate	e .024	< .500	.5
AHTN	.86	< .500	.5	Metolachlor	< .500	< .500	.5
Anthracene	< .500	< .500	.5	N,N-diethyltoluamide (DEET)	8.2	< .500	.5
Anthraquinone	< .500	< .500	.5	Naphthalene	< .500	< .500	.5
Benzo(a)pyrene	< .500	< .500	.5	NPEO2-total	e 10.000	<5.000	5
Benzophenone	.63	< .500	.5	OPEO1	< 1.000	<1.000	1
beta-Sitosterol	3.1	<2.000	2	OPEO2	e 1.200	<1.000	1
BHA	<5.000	<5.000	5	para-Cresol	22	<1.000	1
Bisphenol A	e .170	<1.000	1	para-Nonylphenol-total	e 13.000	<5.000	5
Bromacil	< .500	< .500	.5	Pentachlorophenol	e .036	<2.000	2
Bromoform	< .500	< .500	.5	Phenanthrene	< .500	< .500	.5
Caffeine	11	< .500	.5	Phenol	e .890	e .480	.5
Camphor	< .500	< .500	.5	Prometon	< .500	< .500	.5
Carbaryl	<1.000	<1.000	1	Pyrene	< .500	< .500	.5
Carbazole	< .500	< .500	.5	Skatol	1.1	<1.000	1
Chlorpyrifos	< .500	< .500	.5	Stigmastanol	e .990	<2.000	2
Cholesterol	9.4	e .640	2	Tetrachloroethylene (PCE)	< .500	< .500	.5
Cotinine	<1.000	<1.000	1	Tri(2-chloroethyl)phosphate	e .150	< .500	.5
Cumene	< .500	< .500	.5	Tri(dichlorisopropyl)phosphate	e .270	< .500	.5
Diazinon	e .089	< .500	.5	Tributylphosphate	< .500	< .500	.5
Dichlorvos	<1.000	<1.000	1	Triclosan	1.3	<1.000	1
d-Limonene	e .190	< .500	.5	Triphenyl phosphate	< .500	< .500	.5
Equilenin	e .032	<5.000	5				

References

Aley, Thomas, 1975, A predictive hydro-logic model for evaluating the effects of land use and management on the quantity and quality of water

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Imes, J.L., and Kleeschulte, M.J., 1995, Seasonal ground-water level

changes (1990–93) and flow patterns in the Fristoe Unit of the Mark Twain National Forest, southern Missouri: U.S. Geological Survey Water-Resources Investigations Report 95–4096, 1 sheet.

For more information contact any of the following:

For water information:
U.S. Geological Survey, District Chief
1400 Independence Road, Mail Stop 100
Rolla, Missouri 65401
(573) 308-3664 or "http://mo.water.usgs.gov".

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