

sphere are much lower than 50°C, the fine ash remains in the stratosphere for a long time and is also exposed to intense sunlight. Both processes would lead to significant photodesorption of COS and CS<sub>2</sub>. We therefore conclude that volcanic ash may provide a mechanism by which large amounts of COS, CS<sub>2</sub>, and other trace gases are transported and eventually released into the upper atmosphere.

It is still very difficult to estimate the quantities of sulfur gases that are injected into the stratosphere by these natural explosive volcanic events. Lazrus *et al.* (3) estimated that the sulfur burden in the form of sulfate in the lower stratosphere increased by approximately  $0.5 \times 10^9$  kg after the Fuego eruption in October 1974. If the total COS and CS<sub>2</sub> concentration at the center of the plume was about 5 parts per million by volume (ppmv), then a 30-km<sup>3</sup> volumetric gas flow into the stratosphere would carry the  $0.5 \times 10^9$  kg of sulfur. This magnitude of transport into the stratosphere is possible, especially from the major eruption of Mount St. Helens on 18 May 1980. This mechanism would carry COS and CS<sub>2</sub> as well as SO<sub>2</sub>, which could be converted to sulfate aerosol by photochemical processes (4), enhancing the Junge layer.

R. A. RASMUSSEN  
M. A. K. KHALIL  
R. W. DALLUGE

Department of Environmental Science,  
Oregon Graduate Center,  
19600 N.W. Walker Road,  
Beaverton 97006

S. A. PENKETT  
B. JONES

Environmental and Medical Sciences  
Division, Atomic Energy Research  
Establishment, Harwell,  
Oxon OX11 0RA, England

#### References and Notes

1. A. W. Castleman, H. R. Munkelwitz, B. Manowitz, *Tellus* 26, 222 (1974).
2. —, *Nature (London)* 244, 345 (1973); R. D. Cadle *et al.*, *J. Geophys. Res.* 84, 6961 (1979).
3. A. L. Lazrus, R. D. Cadle, B. W. Gandrud, J. P. Greenberg, *J. Geophys. Res.* 84, 7869 (1979).
4. P. J. Crutzen, *Geophys. Res. Lett.* 3, 73 (1976).
5. N. D. Sze and M. K. Ko, *Nature (London)* 280, 308 (1979); F. J. Sandalls and S. A. Penkett, *Atmos. Environ.* 11, 197 (1979).
6. P. V. Hobbs, L. F. Radke, M. W. Eltgroth, D. A. Hegg, *Science* 211, 816 (1981).
7. T. J. Casadevall and L. P. Greenlands, "Chemistry of gases from Mt. St. Helens," *U.S. Geol. Surv. Prof. Pap.* (1981).
8. J. Momot, *Bull. Soc. Linn. Lyon* 33, 326 (1964).
9. We thank the many colleagues who encouraged us and contributed to this work. We thank T. Casadevall, D. Johnston, and D. Joseph who collected samples. Support for this work was provided by grants ATM7806628 and ATM7809711 from the National Science Foundation, the Chemical Manufacturers Association, and the United Kingdom Department of the Environment.

28 August 1981; revised 26 October 1981

## Radium-226 and Radon-222 in the Coastal Waters of West Florida: High Concentrations and Atmospheric Degassing

**Abstract.** On the central portion of the west Florida continental shelf, radionuclide activities show unusually wide variations: radium-226 activities up to 350 disintegrations per minute per 100 liters, radon-222 activities up to 1300 disintegrations per minute per 100 liters, and deficiencies of radon-222 as low as -10 disintegrations per minute per 100 liters. Florida's phosphate-rich strata seem to be the principal source of the radionuclides, with the transfer occurring directly from sediments or indirectly in streams, ground-water flow, and geothermal springs. Winter storm fronts may enhance radon degassing in the shelf waters.

Neritic waters undergo important processes affecting radium and radon. Rivers carry <sup>226</sup>Ra to the sea in dissolved or adsorbed form (1-3). Interaction with seawater desorbs particulate radium and increases the effective delivery of dis-

solved radium by some rivers (1, 4) through a mechanism resembling the desorption of barium (5). Waters of the continental shelf off southern California are enriched in <sup>226</sup>Ra resulting from either upwelling or release from sediments

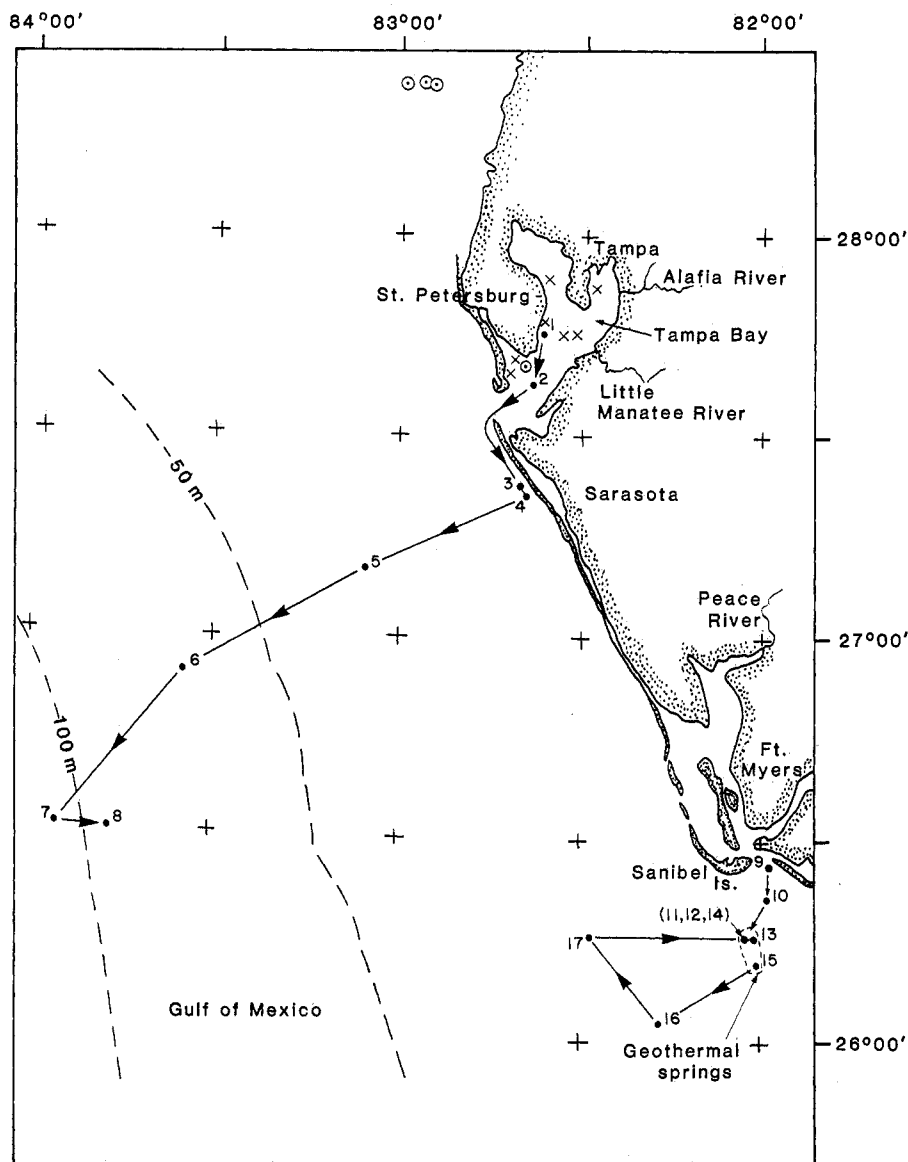


Fig. 1. Stations occupied during the 14-month investigation of radium and radon on the west-central Florida shelf: ●, stations for the cruise in March 1980, with arrows showing the cruise track; ○, stations for the cruise in September 1980; x, Tampa Bay stations sampled in February 1981.

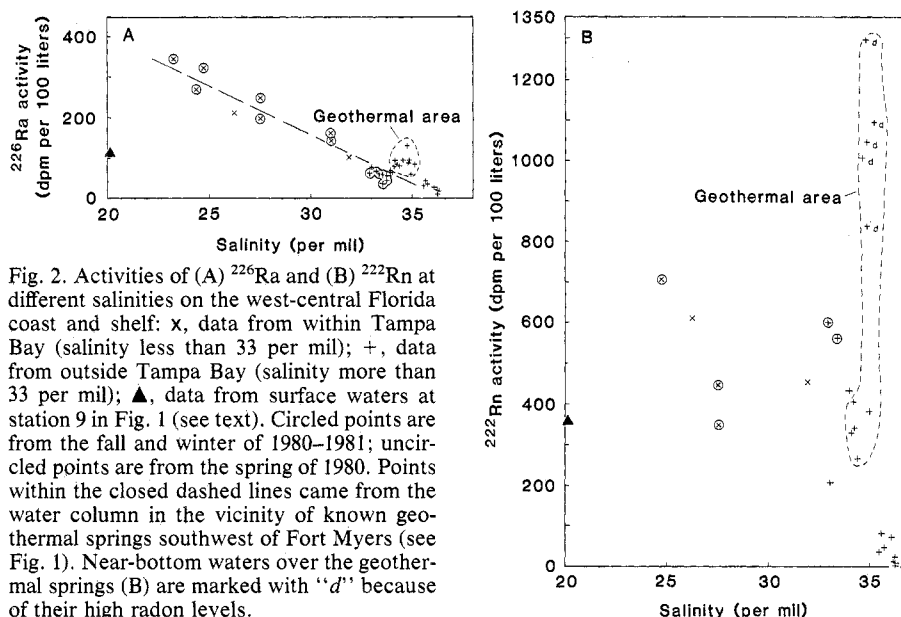


Fig. 2. Activities of (A)  $^{226}\text{Ra}$  and (B)  $^{222}\text{Rn}$  at different salinities on the west-central Florida coast and shelf: x, data from within Tampa Bay (salinity less than 33 per mil); +, data from outside Tampa Bay (salinity more than 33 per mil); ▲, data from surface waters at station 9 in Fig. 1 (see text). Circled points are from the fall and winter of 1980–1981; uncircled points are from the spring of 1980. Points within the closed dashed lines came from the water column in the vicinity of known geothermal springs southwest of Fort Myers (see Fig. 1). Near-bottom waters over the geothermal springs (B) are marked with “d” because of their high radon levels.

(6). In the bottom 10 m of water in the New York Bight, excess radon seems to be strongly released from clay-rich sediment (7).

Few determinations of radium and radon have been made on the continental shelves of the Gulf of Mexico. Reid (8) measured  $^{228}\text{Ra}/^{226}\text{Ra}$  activity ratios near the shelf break of the northwestern Gulf and  $^{226}\text{Ra}$  activities in a Texas bay. In Gulf surface waters, the  $^{228}\text{Ra}/^{226}\text{Ra}$  ratio seems to have increased in 5 years (9), but involvement of the shelf or its sediments has not been demonstrated. Information is very scarce about radium and radon on the west Florida continental shelf which, with an area of 178,000 km<sup>2</sup>, is a major feature of the Gulf and an important shelf environment of the North American continent.

Therefore, in March of 1980 we began a 14-month investigation of  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$  in fresh waters and coastal marine waters of west-central Florida (Fig. 1). Three important conclusions emerged. First, these shelf waters are highly enriched in  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$  as compared to other U.S. coastal waters, with the Florida phosphate beds being a likely source. Second, both nuclides are supplied by geothermal springs to shelf waters southwest of Fort Myers, Florida (10); radon activities are especially enhanced by this mechanism. Third, the passage of winter storm fronts across the shelf appears to produce radon degassing to the atmosphere that rivals the most intense degassing found as a result of the Geochemical Ocean Sections Study (GEOSECS) expeditions.

Data for the marine portion of our study were obtained on two cruises in 1980 (March and September) and on half-

day sampling trips around Tampa Bay in 1981 (Fig. 1). Ancillary data on west Florida runoff were obtained from the Apalachicola, Suwannee, Peace, Little Manatee, and Alafia rivers. The Apalachicola River is located in northwestern Florida; the Suwannee River enters the Gulf of Mexico about 150 km north of Tampa; the Peace River enters the Gulf between Sarasota and Fort Myers; and the Alafia and Little Manatee rivers enter Tampa Bay (Fig. 1).

After sample collection, both  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$  were determined to within 5 to 10 percent by the radon-emanation method (11); for some of the samples radium was first extracted onto manganese-coated acrylic fiber (8). In addition, salinities were determined to 0.01 per mil with a Guildline Autosol conductometric salinometer.

The outstanding feature of the data was the very high activities of  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$  in waters along west-central Florida as compared to other coastal waters of the United States (Fig. 2). In Tampa Bay,  $^{226}\text{Ra}$  activities reached 350 dpm per 100 liters (Fig. 2A), and  $^{222}\text{Rn}$  activities reached 700 dpm per 100 liters (Fig. 2B). Some radon activities near geothermal springs southwest of Fort Myers were roughly twice those in Tampa Bay (Fig. 2B). Station 9 had lower activities of  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$  than Tampa Bay, but its activities were still higher than reported elsewhere. By comparison, the Hudson estuary and New York Bight had  $^{226}\text{Ra}$  activities of only 9.5 to 10 dpm per 100 liters (1, 2, 12), and the plume of the Pee Dee River in South Carolina had  $^{226}\text{Ra}$  activities of 10 to 20 dpm per 100 liters (4). Possibly Trinity Bay, Texas, had values closest to our  $^{226}\text{Ra}$  activities:

50 to 100 dpm per 100 liters (8). Data on coastal radon activities are scarce, but the New York Bight had values on the order of tens of disintegrations per minute per 100 liters, ranging upward to 140 dpm per 100 liters (12). In agreement with data from pelagic surface waters (8, 9, 13), offshore waters with salinities of 36.0 per mil or more had low activities of  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$ , about 10 dpm per 100 liters (Fig. 2).

The most probable reason for the high activities of radium and radon in west Florida's estuaries and coastal waters is the mineralogy and stratigraphy of west-central Florida (14). Immediately east of the area shown in Fig. 1 is a region with two shallow formations rich in phosphate deposits and associated uranium [50 to 200 parts per million (ppm) as compared to 3 ppm in normal crustal rocks]. Those two formations, the Bone Valley and Hawthorn, are sources of radium and radon (14). Ground water in the region leaches radium out of those formations to such an extent that local wells can have  $^{226}\text{Ra}$  activities of 1000 dpm per 100 liters or more. The formations are mined for phosphate in many places, and, during processing of the ore, radium tends to concentrate in a gypsum residue that is then left in massive piles exposed to rain. Streams in the phosphate areas have enhanced activities of  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$  as compared to normal surface runoff, and mining may augment the enrichment locally. For example, all of the riverine  $^{226}\text{Ra}$  activities except that of the Apalachicola River were much higher than 10 dpm per 100 liters, a value typical of other U.S. rivers such as the Hudson (1, 2), the Pee Dee (4), and the Mississippi (3) (Table 1).

Details of the mechanisms by which  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$  are transferred from the formations to coastal and estuarine waters are somewhat obscure at present. The nuclides no doubt enter in local streams, as indicated by the enriched activities in Table 1. However, streams may not be the only transport mechanism. The  $^{226}\text{Ra}$  activities in Tampa Bay are larger than those in many west Florida rivers, including one which discharges into Tampa Bay (the Little Manatee River). Thus additional  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$  may come from the seepage of ground water into coastal and estuarine waters and from the leaching of deposited sediment. The relative inputs by the various transport mechanisms are undetermined.

However, there is one well-defined source of radium and radon on the shelf southwest of Fort Myers (Fig. 1): geothermal springs (10). With  $^{226}\text{Ra}$  activi-

ties of 8000 to 11,000 dpm per 100 liters and  $^{222}\text{Rn}$  activities of 88,000 to 96,000 dpm per 100 liters, the heated seawater discharging from those springs is enormously enriched as compared to the shelf background. Spring waters have salinities of 34.9 to 35.1 per mil, and they inject pulses of radionuclides that can be detected in the overlying water (see in Fig. 2 clusters of points labeled "geothermal area"). The radon pulse is particularly noteworthy. Five near-bottom samples taken within a 3-km<sup>2</sup> area with known springs showed  $^{222}\text{Rn}$  activities of 800 to 1300 dpm per 100 liters, much higher than any reported oceanic values known to us. The surrounding shelf waters in nonspring areas had  $^{222}\text{Rn}$  activities of less than 100 dpm per 100 liters (see lower right-hand corner of Fig. 2B).

There was also a measurable enhancement of  $^{226}\text{Ra}$  activity in the water column overlying the springs (see Fig. 2A). Both enhancements were detectable despite a 100-fold dilution of spring water, from 10,000 dpm per 100 liters to about 100 dpm per 100 liters for  $^{226}\text{Ra}$  and from 90,000 dpm per 100 liters to 1000 dpm per 100 liters for  $^{222}\text{Rn}$ .

After release to coastal waters, radium and radon from west Florida sources may undergo several processes. Simple conservative mixing with shelf waters would reduce the measured activities in proportion to the salinity increases, as seemed to occur to  $^{226}\text{Ra}$  from Tampa Bay out across the shelf (Fig. 2A). Radon-222 in upper waters can be lost to the atmosphere as elsewhere in the ocean (13). This degassing process may

be enhanced by storms such as the major fronts that move southeastward across the Gulf of Mexico with an average frequency of four per month (15).

Radon depletion was observed during the March cruise (Fig. 1 and Table 2). At that time Tampa Bay had very high excess radon activities (16) as did the near-shore coastal waters down to station 9 and over the geothermal springs at stations 11 through 15. However, as we steamed westward, the ship encountered a strong winter storm front near station 5. The storm reached its maximum near station 6 with winds of 20 to 25 knots (37 to 46 km/hour) and waves 1 to 2 m high. Remnants of the front and its turbulence were still present at stations 7 and 8. Coincidentally, shelf waters at stations 5 through 8 showed sizable  $^{222}\text{Rn}$  deficiency

Table 1. Activities of  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$  in Florida rivers entering the Gulf of Mexico.

River	Drainage area	Sample location	Activities (dpm per 100 liters)	
			$^{222}\text{Rn}$	$^{226}\text{Ra}$
Apalachicola	Northwest Florida, no phosphate deposits	At 110 km upstream from mouth	411	14
Suwannee	Phosphate region, north-central Florida	At 38 km upstream from mouth	6,590	210
Peace	Phosphate region, central Florida	At 25 km upstream from mouth	12,000	100
Peace	Phosphate region, central Florida	At 35 km upstream from mouth	9,110	91
Alafia (17)	Phosphate region, west-central Florida	At 8 km upstream from mouth		375
Alafia (17)	Phosphate region, west-central Florida	At mouth by fertilizer plant on Tampa Bay		555
Little Manatee	Phosphate region, west-central Florida	At 10 km upstream, salinity < 1 per mil	9,100	186

Table 2. Surface and near-bottom activities of the unsupported  $^{222}\text{Rn}$  for the estuaries and shelf waters of west-central Florida. Station locations are given in Fig. 1. Salinities indicate the approximate contributions of shelf waters (36.2 per mil) and estuarine waters (0 to 33 per mil).

Station number	Water depth (m)	Surface waters				Deeper waters			
		Sample depth (m)	<sup>226</sup> Ra (dpm/100 liters)	Unsup-ported <sup>222</sup> Rn* (dpm/100 liters)	Salinity (per mil)	Sample depth (m)	<sup>226</sup> Ra (dpm/100 liters)	Unsup-ported <sup>222</sup> Rn* (dpm/100 liters)	Salinity (per mil)
Cruise (March 1980)									
1	6	~3	213	397	26.26				
2	8	~3	104	349	31.94				
3	8	~3	69		33.91				
4	8	~3	67	366	34.00				
5	31	4	22	-8.3	36.21	25	27	44.3	36.08
6	57	5	20	-9.9	36.28	47	26	-1.3	36.25
7	103					50	11	-4.6	36.21
7	103					95	16	-3.7	36.29
8	76	2	11	-2.6	36.20	42	11	4.7	36.25
9	3	2	112	246	20.04				
10	6	3	74	133	33.02				
11	13	1	78	252	34.12	10	95	914	34.59
12	13	3	92	314	34.15	10	87	752	34.81
13	14	3	84	256	34.27	12	95	953	34.85
14	18	5	80	186	34.37	15	132	1171	34.74
15	15	9	60	323	34.96	14	84	1012	35.14
16	20	6	38		35.66	16	36	13	35.71
17	20	5			35.49	15	32	53	35.58
Tampa Bay (February 1981)									
	6	~2	323	384	24.72				
	6	~2	249	197	27.51				
	8	~2	198	151	27.56				
	8	~2	64	536	32.94				
	8	~2	60	502	33.35				

\*This quantity is the activity of  $^{222}\text{Rn}$  minus the activity of  $^{226}\text{Ra}$  present in the same sample.

cies. At stations 5 and 6 the deficiencies were especially pronounced, reaching values nearly 10 dpm per 100 liters lower than parent  $^{226}\text{Ra}$  activities. Radon deficiencies at stations 7 and 8 were measured after the main front had passed and were smaller, although considerably deeper, than at stations 5 and 6.

Radon depletions found on the west-central Florida shelf resembled or exceeded the most intense radon degassing reported by the GEOSECS expeditions (13). At 29 GEOSECS stations in the Atlantic and Pacific, the maximum depth of radon depletion was 50 to 90 m; the west-central Florida shelf had depletions at depths of 50 to 95 m. However, maximum GEOSECS radon deficiencies were about -6 dpm per 100 liters, whereas the west-central Florida shelf showed substantially greater radon depletions. But the percentage depletions of  $^{222}\text{Rn}$  below equilibrium with its parent  $^{226}\text{Ra}$  were reasonably similar for the two data sets. Using values from Table 2, we found that the maximum percentage depletions at stations 5 through 8 were 24 to 50 percent, which fall in the middle of the GEOSECS range for maximum percentage radon depletion: 10 to 70 percent (average value, 29 percent).

To be certain of the cause of the high radon degassing on the west-central Florida shelf, one would need more hydrographic and circulation data than are currently available. However, it is quite reasonable to suggest that the storm front encountered on the March cruise played an important role by enhancing turbulence, gas exchange, or the sinking of radon-deficient surface waters. Since the standing crops of  $^{222}\text{Rn}$  on the west-central Florida shelf are much larger than reported elsewhere in the ocean, it is also possible that storms across the shelf produce a larger transport of radon to the atmosphere per unit area of sea surface than found elsewhere.

KENT A. FANNING  
JABE A. BRELAND II  
ROBERT H. BYRNE

Department of Marine Science,  
University of South Florida,  
St. Petersburg 33701

#### References and Notes

1. Y. H. Li, G. Mathieu, P. Biscaye, H. J. Simpson, *Earth Planet. Sci. Lett.* **37**, 237 (1977).
2. D. E. Hammond, H. J. Simpson, G. Mathieu, *J. Geophys. Res.* **82**, 3913 (1977).
3. W. S. Moore, *Earth Planet. Sci. Lett.* **2**, 231 (1967).
4. R. J. Elsinger and W. S. Moore, *ibid.* **48**, 239 (1980).
5. J. S. Hanor and L. H. Chan, *ibid.* **37**, 242 (1977).
6. K. G. Knauss, T. L. Ku, W. S. Moore, *ibid.* **39**, 235 (1978).
7. P. E. Biscaye, D. R. Olsen, G. Mathieu, in *First American-Soviet Symposium on Chemical Pollution of the Marine Environment*, compiled by

- K. K. Turekian and A. I. Simonov (Publication EPA-600/9-78-038, Environmental Protection Agency, Washington, D.C., 1978), p. 125.
8. D. F. Reid, thesis, Texas A&M University (1979).
9. ———, W. S. Moore, W. M. Sackett, *Earth Planet. Sci. Lett.* **43**, 227 (1979).
10. K. A. Fanning, R. H. Byrne, J. A. Breland II, P. R. Betzer, W. S. Moore, R. J. Elsinger, T. E. Pyle, *ibid.* **52**, 345 (1981).
11. W. S. Broecker, in *Symposium on Diffusion in Oceans and Fresh Water*, T. Ichiye, Ed. (Lamont Geological Observatory, Palisades, N.Y., 1965), p. 116.
12. P. Biscaye, personal communication.
13. A. E. Bainbridge, W. S. Broecker, R. M. Horowitz, Y. H. Li, G. Mathieu, J. Sarmiento, *GEOSECS Atlantic and Pacific Surface Hydrography and Radon Atlas* (National Science Foundation, Washington, D.C., 1977).
14. R. F. Kaufman and D. J. Bliss, *Effects of Phosphate Mineralization and the Phosphate*

*Industry on Radium-226 in Ground Water of Central Florida* (Publication EPA/520-6-77-010, Environmental Protection Agency, Washington, D.C., 1977).

15. W. K. Henry, *Mon. Weather Rev.* **107**, 1078 (1979).
16. Nearly 1 year later, in February 1981, Tampa Bay waters again had high excess radon activities (Table 2).
17. S. Upchurch, personal communication.
18. We thank G. Mathieu and R. Lupton of Lamont-Doherty Geological Observatory for assistance in setting up the radon counting facility at the University of South Florida. We thank P. Biscaye for constructive advice and criticism of the work and the Florida Institute for Oceanography for shiptime aboard the R.V. *Bellows*. Supported under Department of Energy contracts EE-77-S-05-5486, 79EV05486, 80EV05486, and 81EV05486.

11 May 1981; revised 23 November 1981

## Cytoplasmic Calcium in the Mediation of Macula Densa Tubulo-Glomerular Feedback Responses

**Abstract.** Within each nephron of the mammalian kidney, a feedback mechanism operating between the macula densa segment of the distal tubule and the afferent arteriole participates in the regulation of glomerular filtration rate. Retrograde microperfusion studies in rats were conducted to test the hypothesis that activation of macula densa cytoplasmic calcium is involved in the transmission of feedback signals to the vascular elements. Perfusion into distal tubules with a hypotonic solution (70 milliosmolar) elicited moderate decreases in glomerular pressure of  $6 \pm 0.8$  millimeters of mercury. With the addition of a calcium ionophore (A23187) glomerular pressure decreased by  $16 \pm 1.1$  millimeters of mercury. When a solution devoid of calcium but containing A23187 was used, the feedback response was inhibited. Thus, cytoplasmic calcium within the receptor cells may participate in the transmission of feedback signals to the contractile cells.

In each nephron of the mammalian kidney, the macula densa segment of the distal tubule is in close proximity with the vascular elements of its own glomerulus. One intrinsic system regulating renal vascular resistance at the level of the single nephron involves an interaction between these structures. This mechanism has been termed tubulo-glomerular feedback. It is generally considered that the macula densa cells of the distal tubule detect changes in tubular fluid composition and then transmit signals to the glomerular vasculature causing changes in vascular tone (1).

In the tubular fluid flowing by the macula densa cells, the concentration of sodium chloride (NaCl) and the total solute concentration (osmolality) are usually about one-third of the plasma concentrations. As the rate of flow through the loop of Henle increases, the NaCl concentration and osmolality also increase (2). The macula densa cells appear to be responsive to flow-related alterations in the concentration of tubular fluid and, by effecting alterations in the glomerular filtration, participate in the regulation of fluid flow along the nephron. Thus, in response to extrinsic situations that cause increases in glomerular filtration rate (GFR), the fluid flow

rate and tubular fluid electrolyte concentrations at the macula densa increase, thereby leading to feedback-mediated increases in afferent arteriolar resistance and a return of GFR toward normal.

There is some controversy regarding the specific constituent of the tubular fluid that is sensed by the receptor system. Our studies have indicated that the feedback receptor mechanism does not have a specific requirement for either sodium or chloride concentration and that the receptor system may be responsive to the osmolality of the tubular fluid (3). However, other investigators (4) have suggested that chloride concentration is important.

The sequence of cellular events that transmit the signal from the luminal receptor system across the macula densa cells and through the extraglomerular mesangial cells to the vascular contractile elements remains unknown. We reasoned that one means for the transduction of signals by the macula densa cells might involve an alteration in the concentration of an intracellular messenger system. Since previous studies have established the importance of cytoplasmic calcium as a coupling agent in many stimulus-response mechanisms (5), we considered the proposal that intracellular