A lead isotope perspective on urban development in ancient Naples

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Edited by Thure E. Cerling, University of Utah, Salt Lake City, UT, and approved April 7, 2016 (received for review January 21, 2016)

The influence of a sophisticated water distribution system on urban development in Roman times is tested against the impact of Vesuvian volcanic activity, in particular the great eruption of AD 79, on all of the ancient cities of the Bay of Naples (Neapolis). Written accounts on urbanization outside of Rome are scarce and the archaeological record sketchy, especially during the tumultuous fifth and sixth centuries AD when Neapolis became the dominant city in the region. Here we show that isotopic ratios of lead measured on a well-dated sedimentary sequence from Neapolis’ harbor covering the first six centuries CE have recorded how the AD 79 eruption was followed by a complete overhaul of Neapolis’ water supply network. The Pb isotopic signatures of the sediments further reveal that the previously steady growth of Neapolis’ water distribution system ceased during the collapse of the fifth century AD, although vital repairs to this critical infrastructure were still carried out in the aftermath of invasions and volcanic eruptions.

AD 79 Somma-Vesuvius eruption | Pb isotopes | harbor geoarchaeology | Neapolis | paleo-pollution

Urban centers have always been critically dependent on a stable water supply, and ancient cities relying on masonry aqueducts were particularly vulnerable to the disruption of their water distribution system by earthquakes and volcanic eruptions (1). The archaeological record of the major eruption of Vesuvius in AD 79 and its effect on the water supply of Naples, then known as Neapolis, and its neighboring cities illustrates well how efficiently the Roman world was able to mitigate the effects of major disasters on the daily life of its population.

Neapolis: Water Supply and Volcanism

Neapolis and the surrounding region were supplied with water from the Aqua Augusta or Serino aqueduct, built during the reign of Augustus between 27 BC and AD 10 (2, 3). The Augusta was a regional network supplying eight or nine cities, as well as numerous villas, through multiple branches (Fig. 1A): Nola, possibly Pompeii, Acerra, Atella, Neapolis, Puteoli, Cumae, Baiae, and Misenum (2, 4). The total length of the aqueduct, including its branches, was ~140 km. The construction of this monumental hydraulic network helped meet a need to secure the water supply for the strategic region of Campania during a critical period: the establishment of the Principate (2). The aim of the Augusta was to provide water to naval harbors (first Portus Italius and later Misenum) and the commercial harbor of Puteoli, one of the busiest centers of trade in the Roman Empire (5), as well as to cities, coloniae, and villas of influential individuals. At an unknown time between the fifth century BC and the Middle Ages, the Bolla aqueduct (Fig. 1A) was constructed to bring additional water to Neapolis (3).

One of the challenges in maintaining the Augusta and, with it, the integrity of the water supply of the heavily settled area around Neapolis, was counteracting the slow movements of the ground associated with the activity of volcanic systems, known as bradyseism. Roman water distribution systems consisted of large stone or concrete aqueducts, whose water was, in the western half of the empire at least, distributed to fountains and baths, residences, and other buildings by a large network of fistulae, lead pipes of different diameters but typically centimeter-sized. The availability of piped water at Pompeii, and more broadly at all of the cities of the Bay of Naples supplied by the Aqua Augusta, in response to the impacts of the AD 79 volcanic eruption of Somma-Vesuvius, is a matter of debate (6, 7). Interpretations of archaeological evidence from Pompeii itself disagree as to whether the town was receiving any piped water shortly before the eruption, whereas other viewpoints have emphasized the damaging effect of changes in topography preceding the AD 79 eruption on the aqueduct supplying Pompeii (6, 8). Repairs to the aqueduct channels at Ponte Tirone, near where the Pompeii aqueduct may have connected with the Aqua Augusta supplying Naples, have been interpreted as a remediation of the effects of both pre- and post-AD 79 bradyseism on this aqueduct’s performance (3, 6).

Lead Contamination in the Harbor of Neapolis

To investigate the potential disruption of water supply around the Bay of Naples in the wake of the AD 79 eruption, we measured Pb isotopic compositions and elemental concentrations of the harbor sediments of Neapolis (Fig. 1B and C). Stratigraphic sections were made available as part of the archaeological excavation of the ancient harbor of Naples undertaken at Piazza Municipio by...
Ongoing excavation since 2011 allowed us to sample a 5.5-m-long sediment sequence (Fig. 1). These deposits are well dated by archaeological materials (9–13), with better precision than $^{14}$C or optically stimulated luminescence dating, and they record the history of the city during the first six centuries.
CE (Fig. 2). The level corresponding to the AD 79 eruption is located between −485 and −436 cm. The sediment at that level is heterogeneous and easily recognizable by shell debris, abundant fragments of wood, Posidonia, and pottery, as well as large numbers of rolled pumice pebbles (Plinian pumice lapilli fallout) (14).

Lead concentrations in the Neapolis harbor sediments (93–259 ppm) and the enrichment factor (EF$_{\text{Pb}}$) (Table S1) are similar to previous observations of contaminated sediments (15–17), amounting to excesses of Pb relative to natural Pb concentration levels by a factor of 3–5, deemed to signal anthropogenic pollution (15). The lack of significant variations in Pb abundances throughout the core, with the exception of the top 50 cm, shows that uncontaminated preharbor layers have not been found. The lack of a preharbor unit has been attributed to the dredging of the bottom sediments during the late fourth century/middle third century BC (9, 11, 12, 18), which is attested to by scars in the underlying Yellow Tuff bedrock.

Lead isotope compositions were measured on the sediments to separate the local environmental Pb background residing in minerals from the labile imported components. Samples were leached in chloroform and dilute HBr, and Pb isotope ratios measured on the leachates and their residues. The AD 79 layers stand out as a spike in $^{208}\text{Pb}/^{206}\text{Pb}$ in the residues at −469, −461, and −453 cm (N49R, N50R, and N51R) and in the leachates as well (Fig. 2). In the very illustrative plot of $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ (Fig. 3A), the residues form an alignment distinct from the other two alignments defined by the leachates. The three samples of Neapolitan Yellow Tuff substratum of the harbor fall at the lower end of the residue field (Fig. 3A), hereafter referred to as component α (Fig. 3A).

The leachates form two parallel mixing arrays corresponding to two identifiable sets of samples: the “Old Group,” which includes all of the lowermost layers up to sample N45 (−421 cm), and the “Young Group,” which comprises all of the samples above N45 (Fig. 2). The calculated intersections of both leachate arrays with the residue array (star symbols in Fig. 3) suggest that the leachate and the residue contain a common component, probably from a readily leachable mineral phase present in the local watershed, typically carbonate.

We converted the Pb isotope compositions into their Pb model age $T_{\text{mod}}$ and the time-integrated $^{238}\text{U}/^{204}\text{Pb}$ (µ) and $^{232}\text{Th}/^{208}\text{U}$ (κ) ratios (Table S1), using the equations of Albarède et al. (19). The unique information carried by these alternative coordinates relative to those of raw Pb isotope ratios has been demonstrated in several previous studies (see refs. 19–22). Lead model ages $T_{\text{mod}}$ (in million years, Ma) are proxies for the tectonic age of the

![Fig. 2. Downcore variations of $^{208}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, and $^{207}\text{Pb}/^{204}\text{Pb}$ in leachates, $^{208}\text{Pb}/^{206}\text{Pb}$ in residues, and Pb concentrations. The Young Group consists of all of the samples above layer N45, and the Old Group of all of the samples below. The different paleo-environmental units are also indicated (9, 12, 13). The dates supporting the Age Model of the section were provided by archaeological materials (9–13). The tephra unit of the AD 79 event is indicated by red shading. This latter is identified both geochronologically (dark-red shading), by the cluster of the three samples constituting the upper end-member of the unpolluted water mixing line (component α; see Fig. 3); sedimentologically (light-red shading), by specific sedimentological features (pumice stones); and archaeologically, by consistent archaeological dates (i.e., the second and third date from the bottom of the section). The parallel drift of $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ through time toward geologically old Pb reflects an increasing influence of pollution by the Pb pipe network (fistulae) and is a measure of urban development.](https://www.pnas.org/doi/10.1073/pnas.1600893113)
geological provinces where ore deposits are mined. In Europe, $\text{T}_{\text{mod}}$ closely maps the distribution of its Alpine, Hercynian, and early Paleozoic provinces. All of the points falling on both leachate arrays in Fig. 3A have high $^{232}\text{Th}/^{238}\text{U}$ ($\kappa \sim 3.96–3.99$) (Fig. 3B). The Old Group mixing line includes deposits with $\text{T}_{\text{mod}}$ values ranging from 90 to 130 Ma and high $\kappa$ values ($\sim 3.99$) (Fig. 3B), whereas the Young Group mixing line trends toward Hercynian Pb model ages ($\sim 250$ Ma) and slightly lower $\kappa$ values (Fig. 3B).

Comparison of Fig. 3A and B indicates that the radiogenic ends of the leachate arrays correspond to Variscan (Hercynian $\sim 300$ Ma) lead. Variscan tectonic units are unknown in central and southern Italy (with the exception of Calabria), which have been geologically shaped by the Miocene Apennine orogeny. The Pb component (β) (Fig. 3) is therefore necessarily exotic to the Neapolis area.

Impact of the AD 79 Eruption of Vesuvius as Revealed by $^{206}\text{Pb}/^{204}\text{Pb}$ and $\kappa$

The separation of the isotopic composition of the local vs. imported Pb components in the sediments is especially striking in Fig. 3B, which shows the $\kappa$ parameter as a function of the apparent Pb model age. Factor analysis (Fig. S1) of bulk sediment element abundances identifies Pb as a loner with a large loading on the second factor and clearly separated from other elements indicative of human activity, notably Sn, Ag, and Cu. The particular status of lead is because of the fact that, like many Roman cities—and in particular nearby Herculanum, Pompeii, Puteoli, Cumae, Baiae, and perhaps Misenum too (3, 17, 23, 24)—Neapolis received drinking water through a network of lead pipes. Because Variscan ages are essentially unknown in Peninsular Italy, the Variscan model ages of the anthropogenic component present in the sediment leachates document that contamination

![Fig. 3.](image-url)

(A) Plot of $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ for leachates and residues from the ancient Neapolitan harbor deposits. Neapolitan Yellow Tuff (open circles), travertine (filled squares), and fistulae (filled triangles) (21, 23) are also shown. The residues define a mixing line between a volcanic component best represented by the Neapolitan Yellow Tuff and a natural fluvial (soluble) component represented by the star symbols. The leachates define two well-separated fields, which both can be accounted for by a mixture between a fluvial component and the imported (anthropogenic) component β. (B) Similar plot using the geochemically informed parameters $\kappa (^{232}\text{Th}/^{238}\text{U})$ and tectonic model age $\text{T}_{\text{mod}}$ of the lead sources. This plot shows that the imported Pb component β is of Variscan (Hercynian, $\sim 300$ Ma) age: such values of $\text{T}_{\text{mod}}$ are unknown in peninsular Italy, demonstrating that this component reflects massive contamination of the harbor by lead from the water distribution system. The two groups of $\kappa$ values are distinct, which indicates that a new network of Pb fistulae was installed in the wake of the Somma-Vesuvius AD 79 eruption.
originated primarily from the lead used for the *fistulae* of the local water distribution system (2, 3, 17), even if other lead artifacts may also have contributed to a lesser degree. Similar lead contamination of drinking (“tap”) water by the urban distribution system has been documented in ancient Rome (21) and Pompeii (17) as well.

With the possible exceptions of Pompeii and Herculanum, all these networks were linked to the Aqua Augusta (2), but the distribution tank (*castellum dividatorium*) diverting water to Naples has not been preserved. Masonry from the aqueducts themselves is unlikely to have contributed significant lead to the Neapolis harbor deposits. Considerable survey (reviewed in ref. 3) and geochemical analysis (17) have failed to find any remains of lead pipes or fittings within the main line channel of the Aqua Augusta or in the Bolla aqueduct, consistent with such fittings—known from other Roman aqueducts (25–27)—having been temporary (28) or removed later for recycling (29).

The Variscan $T_{\text{mod}}$ and high $k$ values of component $\beta$ at the radiogenic end of the leachate mixing lines (Fig. 3) clearly place the pre-AD 79 Pompeii harbor leachates at the end of the Neapolis harbor deposits. Whether radiogenic end of the leachate mixing lines (Fig. 3) clearly place the pre-AD 79 Pompeii harbor leachates is very similar to the average of the imported component— argued for a stable source. The imported component $\beta$ change in $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ isotope ratios with time (Fig. 2) attests to a steady increase of the imported component, even through the AD 79 eruption, until $\sim 25$ cm (the first half of the fifth century AD) (Fig. 2). The Vesuvius eruption nevertheless shows a shift of $^{208}\text{Pb}/^{204}\text{Pb}$ relative to $^{206}\text{Pb}/^{204}\text{Pb}$ (Fig. 2). This trend reflects the expansion of the *fistulae* system, either by expanding the network of pipes servicing existing areas or expanding the network to new areas (urban development). The end of this trend is contemporaneous with, and explained by, the final breakdown of the Aqua Augusta between AD 399 (the last mention of the aqueduct in a textual source, *Codex Theodosianus* 15.2.8) and AD 472 and the administrative and economic collapse in Campania accompanying the *Vandal* (AD 410–411), *Varia* (AD 455–463) invasions, plague (AD 467), and the next Plinian eruptions of Vesuvius (AD 472 and AD 512) (2, 3, 36–38). The resulting overall decline in imported lead shows a saw-tooth evolution, with two sharp reductions starting at $\sim 25$ cm (the second half of the fifth century AD) (Fig. 2)—probably following the Plinian eruption—and $\sim 146$ cm (the first half of the sixth century AD) (Fig. 2), coinciding with the sacking of Neapolis by Belisarius (AD 536) and then Totila (AD 542) during the Gothic Wars (39). It is quite remarkable that each sharp drop in the imported Pb component (*fistulae*) is followed by a slow relaxation marking the return of Pb-contaminated waters (Fig. 2), a clear sign that a reduced peri-urban water distribution system was brought back to use, perhaps consisting of lead pipes carrying rainwater or, in the low-lying areas of the town, the water of the Bolla aqueduct.

The dramatic decreases show that these repairs were much slower and of more limited extent than those in the aftermath of the AD 79 eruption, reflecting the comparatively much weaker administration and resources of the fifth-century Bay of Naples.

The last shift in Pb isotopic composition (Fig. 2) of the harbor deposits shows that an increase in Pb contamination occurred at the end of the sixth century AD. A stamped lead pipe dated to the seventh century, found in 2003 near the ancient harbor of Naples (40), records its donation by a member of the town’s elite (41), suggesting renewed attention to the water distribution system of Neapolis, occasioned by the expanding territory and power of the town and possibly an influx of inhabitants from neighboring declining towns (42).

Materials and Methods

We sampled the stratigraphic section of Neapolis’ ancient harbor at high resolution by taking a total of 61 samples (one sample every 9 cm). The samples were analyzed for Pb concentrations and isotopic compositions by MC-ICP-MS and multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) at the Ecole Normale Supérieure de Lyon (Table S1).

Pb Concentrations. Sample dissolution and other manipulations were carried out in a clean laboratory under laminar flow hoods. After sieving at 63 μm, aliquots of 100-mg sediment (fraction < 63 μm from the stratigraphic sections) were dissolved in a 3:1 HCl:HNO3 mixture of concentrated double-distilled HF, HNO3, HClO4 in Savillex beakers and left on a hotplate at 120–130 °C for 8 h, then evaporated to dryness. Perchlorates and any remaining fluorides were converted to chlorides by drying down with distilled 6 M HCl. The
samples in solution in 6 M HCl were all clear, attesting to complete breakdown of the sediments. The samples were redissolved in 2-ml concentrated double-distilled HCl over which ~10% aliquots were further diluted to 0.5 M HNO₃, and to which internal standards were added (2 ppb In). Lead concentrations were analyzed by Q-ICP-MS (Agilent 7500 CX). The upper limit of the blank contribution was a factor of 100,000 smaller than the sample Pb contents.

**Pb Isotope Compositions.** Alliquots of 500-μg sediment (to ensure that the sample Pb contents.

Before Pb separation for Pb isotopic analysis, the residues were attacked in the same manner described above for elementary Pb concentration measurement. The amounts of Pb extracted from all samples were large (>1 mg) and orders of magnitude above the total procedural blank of 

**ACKNOWLEDGMENTS.** We thank Daniela Giampaola and Vittoria Carsana for critical information on harbor basin stratigraphy, Philippe Telouk for ensuring that instruments were always at their best, and the ‘Soprintendenza Speciale per i Beni Archeologici di Napoli e Pompei’ for the possibility to work in the ancient harbor of Naples and the use of the photo in Fig. 1 of the local harbor stratigraphy. Macquarie University and Dr. Bill and Mrs. Janet Gale provided financial support for the collection of the travertine samples. The Young Scientist Program of the Agence Nationale de la Recherche (CNRS) (ANR 2011 JSH3 002 01) and the Roman Mediterranea Ports program (ERC) (102700) provided financial and logistic support; and the Institut National des Sciences de l’Espace provided the analytical facility at the Ecole Normale Supérieure de Lyon.


