

TRANSFER OF MERCURY INTO ALLUVIONS FROM A RIVER : EFFECT OF MERCURY-BEARING SLUDGES ON THE QUALITY OF GROUNDWATER IN THE REGION OF CERNAY, ALSACE.

T.D. DINH, P. MUNTZER and L. ZILLIOX

Institut de Mécanique des Fluides de l'Université Louis Pasteur, Strasbourg (F)
ERA CNRS 0594

S. RAMON

Agence de Bassin Rhin-Meuse, Metz (F)

ABSTRACT

The experimental work exposed in this paper refers to the study of the possibilities for mercury to migrate from river sediments, where it remains accumulated, to neighbouring groundwater, the use of which is planned for drinking water supply.

With the monitoring of the quality of river water and groundwater, notably on a site equipped with piezometers and with a catchment well, the research effort was centered on experimenting in the laboratory. Mercury-bearing sludges, taken in the river, were placed in columns of porous materials, and the leaching of mercury by natural and modified infiltrated water (addition of sodium chloride or hypochlorite) has been studied. When for natural waters, the appearance of mercury at the outlet of the columns is restricted to the initial phase of flow, a large increase of the oxidizing power of water may durably mobilize mercury at high concentrations (up to 100 ppb). Tests effected on sand columns with the presence of clays enabled to appreciate the retention possibilities of the so mobilized mercury.

A discussion of the whole results shows that the risk of pollution with mercury lies in a protracted modification, due to an accidental cause, of river water which supplies the aquifer.

INTRODUCTION

The danger resulting from the contamination with mercury is presently well known throughout the world. Among the vehicles of pollution with mercury, water plays a very important role, either in a direct way (drinking water), or indirectly (food chain).

As mercury is a highly toxic element, - this point being illustrated by the two best known dramas of Minamata (1953) and Niigata (1960) in Japan, - very severe standards have been formulated for this metal in industrialized countries, chiefly

in relation with the consumption of fish and of drinking water (potability threshold = 1 ppb for WHO and EEC, 2 ppb for USA).

In Alsace, the water of the river Thur below Thann has for decades received discharges of dissolved mercury salts ; the condition of the raw water of this stream has improved since the discharges stopped 1973 ; but the effects of the accumulation of mercury in the sediments constitute a problem which is still to be solved. In order that the aquifer may be exploited as a source of drinking water in the neighbourhood of the river, it is necessary to know the possibilities for mercury to migrate into alluvions, starting from these sediments (mercury-bearing sludges), at the same time in to-day's conditions and in the case of an alteration of the quality of river water (either after an accidental discharge, or following the treatment of presently discharged effluents).

This paper stresses the experiencing on columns of porous materials in the laboratory ; the monitoring of the site is presented together with a tentative to generalize the obtained results. The detailed study of this regional problem has been the object of internal reports under an agreement between the Agence de Bassin Rhin-Meuse and the Institut de Mécanique des Fluides de Strasbourg.

EXPERIMENTS ON COLUMNS IN THE LABORATORY

The objective of these experiments is the study of the elementary mechanisms of the transfer of mercury between a fluid phase and a solid phase in a saturated porous medium.

Experimental conditions

Two types of plexiglas columns were used for percolation tests ; with a same length (1 metre), they have an inside diameter of 0.09 and 0.05 m respectively.

The circulation of the fluid is secured by peristaltic pumps ; the flows can be adjusted between 2×10^{-8} and 7×10^{-7} cu.m/s.

Figure 1 illustrates the principle of the experimental unit and of the execution of tests. Water and mercury-bearing sludges collected on the site are brought into intimate contact in Column 1 ; the second column is used to observe the action of a given porous medium (sand alone or sand + clay) on a mercury-bearing water.

The samples of water collected at the outlet of columns have generally a volume of 0.5 litre ; their mercury content is determined by flameless atomic absorption, in the Laboratoire d'Hydrologie de la Faculté de Pharmacie de Strasbourg. (Every value lower than 0.2 ppb is considered as not significant).

The porous media are constituted, for Column 1, of quartz sands, a part of which is mixed with mercury-bearing sludges ; for Column 2, of sands of the same type, with or without addition of clays (kaolinite, montmorillonite). The sands had a mean diameter of 0.5, 0.2 or 0.1 mm.

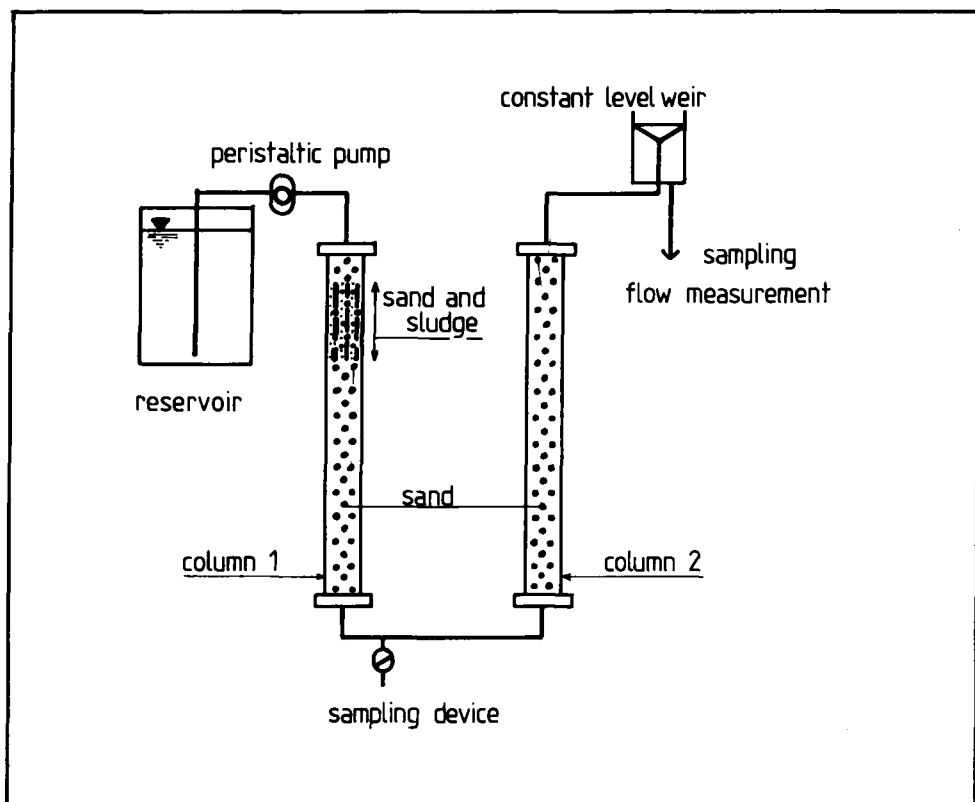


Fig. 1. Diagram of the test unit.

The percolating fluids are of three types :

- natural waters, coming either from the Strasbourg distribution system, or from the river (Thur) at the studied site,
- mercury-bearing waters from a manufacture, and diluted with groundwater from the site,
- modified natural waters, obtained by adding sodium chloride or sodium hypochlorite to river water.

Experimental results

As preliminary tests had shown that filtering of natural waters through the utilized quartz sands did not allow traces of mercury to appear at the outlet, two series of experiments were effected :

- the first one groups percolation tests through columns containing mercury-bearing sludge (Column 1, Fig. 1),
- the second groups percolation tests of mercury-bearing water through columns of porous material (sand or sand + clay).

First test series. For a natural water without mercury, flowing through Column 1, one may observe at the outlet a first and short appearance of mercury at the beginning of filtration (contents lower than 2 ppb), followed by a distinct decrease of the concentration down to values which are no more significant (lower than 0.2 ppb). The quantity of mercury extracted from these tests is extremely low : about 1/1000 of the one contained in sludge. Figure 2 illustrates this behaviour with one of the tests.

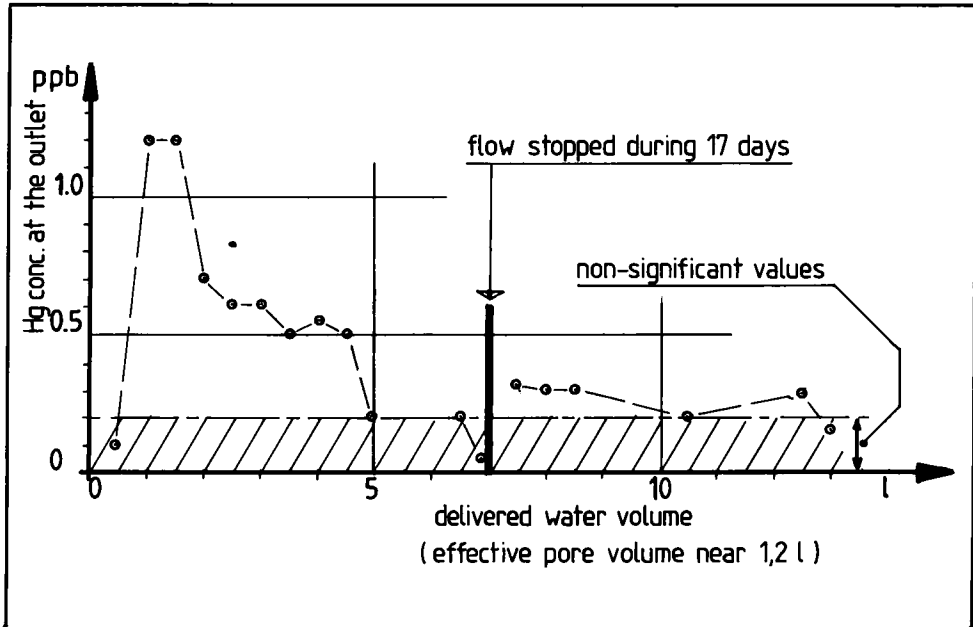


Fig. 2. Mercury concentration at the outlet of Column 1 . Percolating fluid : natural water

Note : it has been observed that this mobilization of mercury can be momentarily altered under the action of variations of pressure or flow.

Tests with an addition of NaCl to natural waters, at the inlet of the column, have shown that a salinity lower than 10 g/l has no action on the mobilization of mercury. On the contrary, mercury could be extracted in a notable proportion from sludges, by adding sodium hypochlorite to the natural waters (NaClO amount > 0.1° chl.) ; concentration up to 100 ppb could be obtained with an extended contact.

Second test series. The filtration of water containing mercury bound to suspensions of iron hydroxide leads to a retention of mercury by sand alone. The filtration of water containing mercury (2 to 15 ppb) extracted from sludge under the action of sodium hypochlorite, leads to a far more limited retention : on a column of sand with clays (2 to 5 %), a retention of 20 to 60 % has been observed from the outset of filtration, for a delivered water volume corresponding to about 20 times the pore

space ; mercury can thereafter fast entirely migrate. For instance, in a test with 2 % kaolinite uniformly mixed with sand, one litre of porous material had retained 40 micrograms.

MONITORING OF THE EXPERIMENTAL SITE

From November, 1978 to September, 1979, it consisted to collect every month water samples at several points on a perpendicular to the water course : river, an industrial well working 50 m from the river, and three borings equipped as piezometers, and situated 15, 30 and 150 m from the river.

Mercury contents present strong variations from one month to another, and range chiefly from 0.05 to 0.4 ppb ; 10 % of the values are comprised between 0.5 and 0.7 ppb. When comparing these values with the results obtained in September, 1978, at 10 water catchment points situated less than 100 m from the river, one observes that no value reached the potability threshold (1 ppb) along the Thur.

DISCUSSION OF RESULTS AND OUTLOOK

The work, which comprises at the same time a monitoring of the site and an experimentation on columns, enables to gain a global view concerning the problem of migration of mercury. It is nevertheless useful to remind here the importance of the effect of scale ; in other words, one must not forget that the phenomena, in the nature, are far more complex in space and in time than on the physical model, the interest of which lies in the study of the elementary mechanisms.

It is not possible, with the analytical method which was utilized, to tell in which form mercury has been transferred. Referring to our experiments, and with due consideration of the literature, it still may be admitted that :

- if the mercury present in the percolating fluid exists as a precipitate, i.e. that it is insoluble, it may be retained by simple constituents of the porous medium such as sand ;
- if mercury is bound with very fine suspended matter, a part of it may migrate into a sand medium ;
- if mercury exists in a soluble form (in our tests, the solubilization was due to the action of sodium hypochlorite), it may be transferred through the porous medium. The solubilization obtained in some tests illustrates the results described by Hem (1970), who has shown that the presence of chlorine ion in an oxidizing water favours the solubilization of mercury.

Following proposals are suggested in the management of drinking water :

- if the borings for drinking water supply are situated near a medium polluted with mercury, it is compulsory to examine the characteristics of water and sediments (this is to be done at regular intervals), as well as the structure of the aquifer (fissured or not, grain-size distribution, content in clay or adsorbing complex, etc.) ;

- when controlling an aquifer suspected to be polluted with mercury, water samples must be collected at least every month, so that a significant opinion can be formulated ; a content exceeding 0.5 ppb requires special attention.

In order to gain a better knowledge of the phenomena of transfer and spreading of mercury in soluble forms in aquifers, it is necessary to effect systematic experiments, with a precise control of such parameters as : chemical forms of mercury, physical-chemical characteristics of porous media, flow regimes...

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REFERENCES

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Note : Over 50 references are included in internal reports available at the Agence Financière de Bassin Rhin-Meuse on the diploma work of T.D. Dinh and complementary studies.