A One-Year Systematic Study of Electrodes for Long Period Measurements of the Electric Field in Geophysical Environments

Frédéric E. Perrier¹, Gilbert Petiau², Gérard Clerc³, Vsevolod Bogorodsky⁴, Ercan Erkul⁵, Laurence Jouniaux⁶, David Lesmes⁶, Jim Macnae⁷, Jean M. Meunier⁸, Dale Morgan⁶, Darcy Nascimento⁹, Guido Oettinger¹⁰, Gerhard Schwarz¹⁰,¹¹, Hiroaki Toh¹², Malcolm J. Valiant⁹, Keeva Vozoff¹³, and Oya Yazıcı-Çakın¹⁴

¹Laboratoire de Géophysique, B.P. 12, 91680 Bruyères-le-Châtel, France
²Observatoire de Chambon-la-Forêt, 43540 Chambon-la-Forêt, France
³Centre de Recherches Géophysiques, 58150 Garchy, France
⁴Geoelectromagnetic Research Institute, 14092, POB 30, Troitsk, Moscow Region, Russia
⁵Geoforschungs Zentrum Potsdam, Telegrafenberg A 31 D-14473-Potsdam, Germany
⁶Earth Resources Laboratory, Massachusetts Institute of Technology, MA 02142, Cambridge, U.S.A.
⁷Macquarie University, CRCAMET, 2109 NSW, Australia
⁸Ecole et Observatoire de Physique du Globe, 5, rue René Descartes, 67084 Strasbourg Cedex, France
⁹Department of Geology and Geophysics, Grant Institute, Edinburgh EH9 3JW, United Kingdom
¹⁰Institut für Geophysik und Geologie, Universität Leipzig, Talstr 35, 04103 Leipzig, Germany
¹¹Sveriges Geologiska Undersöknings, Box 670, S-751 28, Uppsala, Sweden
¹²Ocean Research Institute, University of Tokyo, 1-15-1, Minamidai, Nakano-ku, Tokyo 164, Japan
¹³Harbour Dom Consulting, PO Box 596, North Sydney 2059, Australia
¹⁴B. U. Kandilli Observatory and Earthquake Research Institute, 81220 Cengelköy, Istanbul, Turkey

(Received November 1, 1996; Revised April 23, 1997; Accepted April 25, 1997)

Various types of electrodes designed for the measurement of the electric field in the soil or in sea water at periods larger than one minute have been compared in a one-year experiment in Garchy, France. The experiment included more than fifty electrode pairs with liquid or absorbed electrolytes and Pb/PbCl₂, Ag/AgCl, Cu/CuSO₄ and Cd/CdCl₂ metal-ion couples. The electrode parameters were systematically measured in the laboratory and the electrodes were installed in the field to constitute 50-meter long parallel dipoles separated by 2 meters. Pairs of electrodes used for sea measurements were monitored in a salted water vessel. Forty-two potential differences were recorded with a sampling interval of 1 minute between May 1995 and April 1996. When electrodes are compared, large differences are observed in the long term stability as well as in the sensitivity to diurnal variations, rainfall and soil saturation. For measurements in soil, the installation method of the electrodes plays an important role. In salted water, the best performing electrode pair has a drift of the order of 0.1 mV per year. In soil, typical drifts for the best sensors are of the order of 0.2 mV per month in dry soil and 0.5 mV per month in soaked soil. Preferred electrode designs and installation methods, depending on the external conditions or the type of geophysical measurement, emerge from this experiment. In addition to the magneto-telluric field, potential variations which are not electrode or installation effects are observed and attributed to electrical sources in the soil.

1. Introduction

Variations of the electric field with periods larger than one minute have become a subject of intense activity in geophysical research. Long period magneto-telluric (MT) signals are used to probe the lithosphere or the upper mantle conductivity. The electrical spontaneous polarization (SP) has been observed to be associated with volcanic activity (Fujinawa et al., 1992; Zlotnicki et al., 1994; Hashimoto and Tanaka, 1995) and variations with time scales ranging from one minute to several months have been observed before earthquakes (Park et al., 1993). The long term monitoring of SP could therefore be a way to study volcanic eruptions or tectonic phenomena,
and possibly geophysical systems like oil or gas reservoirs or industrial sites such as underground waste deposits.

These applications typically require a measurement stability of the order of one mV/month or better. For periods larger than 1 minute, the noise coming from the electronic amplifiers can be made negligible (Petiau and Dupis, 1980) and the main source of noise comes from the electrodes. This noise may be generated in the electrodes themselves by electrochemical reactions at the metal interface or in the soil in the neighbourhood of the electrodes.

Although the concept of non-polarizing electrodes has been studied for some time (Petiau and Dupis, 1980; Filloux, 1987), the electrode remains a poorly understood geophysical sensor. The fabrication is still a largely undocumented craft and there seems to be no consensus on the performances of the various types of electrodes (Junge, 1990; Larsen, 1992; Erkul and Müller, 1996). Although some systematic studies of the time variations of SP have been undertaken (Ernstson and Scherer, 1986), many phenomena related to the electrochemical contact with the external medium are still unknown.

As some new sensors became ready for tests (Hamano et al., 1984; Bogorodsky and Bogorodsky, 1996; Meunier, 1996; Petiau, 1996), it was decided to undertake a systematic campaign of comparison between the various available electrodes. The experiment took place in Garchy, France, from April 1995 to April 1996.

The purpose of the campaign was to improve our knowledge on electrodes and to quantify the performances of the various instruments in order to identify the best designs. Furthermore, the campaign aimed at identifying the various limiting factors which can affect the measurement of the electric field at periods ranging from one minute to one year, and to propose possible ways for future developments.

In this paper, the experimental procedures and set-up will be described and a first set of results concerning the long term stability of electrodes will be presented. Results on long period magneto-telluric data interpretation and the analysis of data acquired at higher frequencies (1 Hz to 1 kHz) will be the topics of later papers.

2. Description of the Garchy Electrode Experiment

2.1 Electrodes

The main problem in measuring electrical potentials in geophysical environment is the creation of large electrochemical potentials between an electronic or metallic conductor such as the Copper wire going to the recording device, and an electrolytic conductor such as soil or sea water. For example, the potential between a metal rod and the soil can be of several hundreds of mV and can change by hundreds of mV when the humidity of the soil changes. In order to reduce this effect, a non-polarizing electrode consists of an intermediate medium where a metal/metal-ion couple has a potential which is stabilized with a salt of the metal ion having fixed concentration. A high solubility electrolyte like NaCl or KCl is added to obtain a conductive medium when the metal ion salt has a low solubility like AgCl or PbCl₂. One is then left with liquid junction diffusion potential or other types of contact potentials with the soil. These potentials are much smaller (of the order of ten mV) (Harned and Owen, 1958; Petiau and Dupis, 1980).

Practical realisations of these ideas however can be very different and, for the Garchy experiment, more than 20 different designs and more than hundred electrodes were made available (see Table 1). Details on each individual design will be described in a technical report (Clerc et al., 1997, in preparation). Electrodes are identified by three letters refering to the origin, like PHO for Phoenix, CLF for Chambon-la-Forêt, etc... as described in Table 1.

Various metal/metal-ion couples were used: Pb/PbCl₂, Ag/AgCl, Cu/CuSO₄ as well as Cd/CdCl₂. The electrolyte can be contained in a liquid vessel or may be absorbed in kaolinite, plaster or fiber glass composite materials.
Table 1. Overview of the various electrodes used in the Garchy experiment. A reference describing the electrode is indicated when available, otherwise a contact person is given in parenthesis. The number given before the electrode 3-letter name is the number of electrodes available for the tests.

| Metal/Metal-ion Couples | Pb/PbCl₂ | Ag/AgCl | Cu/CuSO₄ | Cd/CdCl₂ |
|-------------------------|----------|---------|----------|----------|
| **Absorbed**             |          |         |          |          |
| Kaolinite absorber       | 16 CLF-K (Petiau, 1996) | 4 BLC (Ruzié, 1996) | 6 STR (Meunier, 1996) | 4 BLC (Ruzié, 1996) |
|                        | 8 CLF-Na (Petiau, 1996) |         |          |          |
|                        | 4 BAB (Petiau)            |         |          |          |
|                        | 2 BLC (Ruzié, 1996)       |         |          |          |
| Kaolinite absorber       | 10 MOS (Bogor., 1996)     |         |          | 4 BLC (Ruzié, 1996) |
|                        | 8 PHO (Phoenix Inc)        |         |          |          |
|                        | 4 GAR (Choquier, 1996)     |         |          |          |
|                        | 2 BLC (Ruzié, 1996)       |         |          |          |
| **Synthetic absorber**   |          |         |          |          |
|                        | 4 IST (Yazici-Çakin)       |         |          |          |
| **Electrolyte**          |          |         |          |          |
| Electrolyte absorber     | 4 TOX (Hamano et al., 1984) |         |          |          |
|                        | 4 BRE (Thomson)            |         |          |          |
| Electrolyte              | 8 LEI (Schwarz)           |         | 8 POT (Erkul) |
| Natural supply of electrolyte |                  |         | 3 KOL (Hoerd) |
|                        | 7 CAM (MIT)               | 2 CGG (Andrieux) |
|                        | 8 POT (Erkul)             | 2 CGG (Andrieux) |
|                        | 8 POT (Erkul)             | 2 CGG (Andrieux) |

Different variants of the same designs were also proposed, as in the case of the Pb/PbCl₂ CLF electrode with kaolinite saturated with KCl (CLF-K) or NaCl (CLF-Na), the latter design being favored for measurements in the sea. The BAB electrode is a preliminary version of the CLF-Na that has been used already for deep sea measurements and has therefore reached the equilibrium concentration of NaCl in the sea (about 30 g/l), in contrast with an original NaCl concentration at saturation of about 360 g/l at 25°C.

For some electrodes (PHO, BLC, STR), the absorbing material is also used for the contact with the soil. For most designs however, it is chosen to restrict the ion exchanges with the outside medium by a low permeability plug such as ceramic, wood (Petiau, 1996), or fiber glass composite materials.

Electrodes with liquid electrolytes tend to loose their electrolyte through the contact interface (usually ceramic plugs) and they have to be provided with a large reservoir (CAM) or with
a refilling system (LEI\textsuperscript{1}, EDI). For deep sea measurements, the outside medium is a stable electrolyte and an option is to use this medium to stabilize the electrode (Filloux, 1987). The TOK (Hamano et al., 1984) and BRE electrodes of the campaign are based on this principle.

The number of electrodes available in each family varied from 2 to 16 (Table 1). The statistical significance of some results has to be taken with care for families with insufficient number of probes.

2.2 Measurements in the laboratory

The self-potentials, the resistance and the temperature coefficients of the electrodes were first measured in the laboratory.

The electrical potential of each electrode was measured in a vessel containing a foam soaked with salted water, with respect to a reference electrode (Ingold Ag/AgCl electrode or one CLF-Na electrode) and with respect to one electrode of each family. Within some families of electrodes, the potential differences are of the order of 1 mV (MOS, TOK, POT, STR, CAM, PHO), or smaller than 0.1 mV (CLF, TOK), indicating that the electrodes are very similar. Other electrodes had potential differences up to several mV (IST, GAR, EDI), or more (BLC) and on that evidence alone can be considered less robust against fabrication imperfections. In the case of the LEI electrodes, initial potential differences were observed with values up to several mV but these values decreased to 1 mV or smaller within 2 weeks.

The resistance of each electrode was measured by measuring the resistance between the electrode and a metal plate on a saline sponge, using an AC ohmmeter at 4 kHz to avoid polarization of the electrode. Some electrodes with high permability contact interfaces (TOK, PHO, MOS) have a low external contact resistance (20 to 40 Ω) and electrodes with restricted contact surface area usually are more resistive (of the order of several hundreds of Ω for LEI or CLF).

The temperature coefficient of the electrode reflects the chemical properties of its components. It depends not only on the metal-ion couple but also on the various salts in contact with the metal, their saturation conditions, and the temperature sensitivity of the solubilities. In the case of Pb/PbCl\textsubscript{2} electrodes, it is possible to minimize the temperature coefficient by cancelling the temperature dependence of the electrochemical potentials (Nernst equation, Harned and Owen, 1958) and the temperature dependence of the salt solubilities (Petiau and Dupis, 1980). The temperature coefficient of Pb/PbCl\textsubscript{2} electrodes is then of the order of 30 μV/°C (CLF-K), 75 μV/°C (MOS) or 200 μV/°C (CLF-Na). The temperature coefficient of Ag/AgCl electrodes is in general larger (160 μV/°C for LEI electrodes or 300 μV/°C for TOK electrodes). Other electrodes used in Garchy tend to have temperature coefficients of several hundreds of μV/°C, with variations of the same magnitude within a same family (Clerc et al., 1997).

When the electrodes are installed in the soil, additional temperature variations can be expected. The temperature dependence of the liquid junction diffusion potential is given by the Henderson equation (Henderson, 1907 or Harned and Owen, 1958), and is of the order of the contact potential divided by the absolute temperature, hence of the order of a few tens of μV/°C (see also Junge, 1990).

The transfer function from 1 kHz to 1000 s and the noise from 10 Hz to 1000 s were also measured on a salted foam in the laboratory. The measurement protocol and the results will be reported in (Clerc et al., 1997).

2.3 Installation of electrodes in the field

As electrodes are sensitive to the physical and chemical evolution of the soil, it is necessary to bury the electrodes for long period measurements. The penetration depth of the diurnal temperature variations in the soil is of the order of tens of cm. Depending on the physical

\textsuperscript{1}The LEI electrode, based on the Ingold/Argenthal electrode, was developed at the Free University, Berlin.
parameters of the soil, rain water can penetrate more than one meter, and introduce additional temperature variations. A depth of the order of one meter or more is therefore desirable. For practical reasons, the electrodes for the Garchy experiment were installed in 50 cm diameter holes at an average depth of 75 cm (Fig. 1).

Two opposite approaches were used for the installation of the electrodes (Fig. 1). In one approach, the electrode is installed in 10 liters of a contact mud obtained by mixing kaolinite and a saturated NaCl solution in water (Fig. 1(a)). This contact mud ensures a good electrical contact with the soil by averaging local electrical heterogeneities. The NaCl salt has also the property of keeping the moisture content stable in the mud, as can be demonstrated by studies in the laboratory (Clerc et al., 1997). To restrict the flow of rain water, one possibility is to put the mud and the electrode in a plastic bucket (Bogorodsky and Bogorodsky, 1996), leaving only the top for electrical contact with the ground (Fig. 1(b)). The bucket is filled with contact mud (PHO in line 39) or local soil with NaCl in excess of saturation (MOS lines 15 and 16). For some electrodes, bentonite (smectite) has been used instead of kaolinite, with or without NaCl.

In a second approach (STR, CAM), the electrode is placed directly in the soil in order not to alter the local chemical equilibrium (Fig. 1(c)).

2.4 Configurations of electric dipoles and data acquisition

The configuration of the electric dipoles is shown in Fig. 2. Two parallel lines of holes, with 2 meters between holes, are separated by 50 meters. Electrodes of each pair are installed in corresponding holes so that the electric potential across a 50 meter dipole is measured. This configuration has been chosen in order to measure the MT signals, and to measure the effects introduced by slightly different soil conditions on the two electrodes of the dipoles. Two 2-meter and one 58-meter long dipoles were also available in the perpendicular direction (Fig. 2).

Electrodes were connected to electrical wires having double insulation and extra mechanical resistance. The connection was soldered and protected by adhesive thermo-retractable sheath. The cables were connected to preamplifiers with gain 50 and installed in a 2.2 meter deep thermally insulated underground vault (Fig. 3). The input impedance of these preamplifiers is 270 MΩ, taking into account the impedance of electrostatic discharge protection devices, with a typical noise peak to peak of 0.6 mV from 1 Hz to DC (Clerc, 1996). The signals were further amplified (gain 10) and filtered (100 s corner frequency).
Fig. 2. The experimental layout of the electric dipoles during the Garchy experiment. Most of the recorded potential differences correspond to 50-meter long dipoles, joining one electrode in a hole of the northern hole line with one electrode in the corresponding hole of the southern hole line. One 58-meter and two 2-meter long dipoles were in the perpendicular direction and are indicated by vertical arrows.
Pairs of electrodes designed for sea measurements (BRE, CLF-Na, TOK, BAB) were monitored in a water vessel (Fig. 3) with NaCl at sea water concentration (30 g/l). A total of 42 electric dipoles were recorded with a sampling time of one minute from May 1995 to April 1996.

The potential difference for each dipole was measured at the beginning of the experiment, immediately after installation. At the end of the experiment, the potential difference of each dipoles was measured again, all electrodes were recovered and their parameters measured in the laboratory with the same procedure as before installation. The comparison of the self-potentials of the electrodes before and after the year spent in the soil permits us to separate potential variations due to the electrodes themselves from installation or soil effects.

The temperature sensitivity of the electronics of all data processing channels were measured at the end of the experiment. The temperature sensitivity is greatest at the level of amplifiers in the laboratory (see Fig. 3), with a measured sensitivity generally smaller than 2 µV/°C, with however three exceptions: one channels at +5 µV/°C, one channel at −4 µV/°C and one channel at −21 µV/°C. The gain factors of all channels were at the nominal value (500) within one percent.

In addition to the 42 electric dipoles, the three components of the magnetic field measured by a fluxgate magnetometer were recorded as well as some meteorological parameters: rainfall, soil humidity at a depth of 50 cm, soil temperatures at 39 cm and 80 cm depth on the south side (Fig. 2), and at 15 cm and 52 cm depth on the north side, as well as the temperatures in the laboratory and in the sea water vessel. The soil moisture is measured by the resistance of a gypsum rod and is expressed in bars as the capillary tension of the soil.

3. Analysis of the Long Term Behaviour

3.1 Results for electrodes in the sea water vessel

The possible sources of potential variation in the sea water vessel are due to the electrodes themselves. Some dipoles (BRE, some versions of BAB) were unstable and showed regular transient changes of potential of order 1 mV. Two dipoles (CLF-Na and TOK) changed by less than 0.4 mV over one year of measurement. One BAB dipole had a regular drift but a smaller noise at shorter time scales.
The three best sea dipoles are compared in Fig. 4. In this figure, the typical linear drift given by a straight line fit is shown as a function of the length of time of the considered data portion. This mode of comparison has been chosen rather than harmonic decomposition because straight line drifts do indeed represent the time evolution of electrodes, which in general reflect a process which has an irreversible nature.

In Fig. 4, the TOK dipole was corrected for temperature variations in the sea water vessel. The TOK dipole indeed showed a small but significant correlation with the measured temperature in the water vessel of about 20 $\mu$V/°C, with a tendency to increase with time.

One can see in Fig. 4 that the TOK and CLF-Na designs have drifts of the order of 0.2 mV or smaller for time scales larger than one month, demonstrating the excellent intrinsic stabilities of these designs. One can also see that the TOK Ag/AgCl electrode has less noise than the CLF-Na electrode by a factor 2 to 3 for the considered time scales. This fact can be understood if the dominating noise source at periods smaller than 10 days is the diffusion noise.

Diffusion noise is due to a gradient of concentration of electrolyte (here NaCl) between the electrode and the external solution (sea). By construction, the CLF electrode is built to limit exchanges of ions and to keep inside the concentration at saturation (360 g/l) as long as possible, and it has a large concentration gradient with the sea water vessel (30 g/l). Conversely, the TOK electrode adjusts itself within a few days to the concentration of the sea water vessel. It is therefore expected that diffusion noise should be present in the case of the CLF-Na electrode, and not in the case of the TOK electrode.

Fig. 4. Typical drifts of dipoles in the salted water vessel as a function of time scale.
As for the BAB electrode, which is a CLF electrode not protected against desaturation and has spent a long time in the sea, its concentration of NaCl has decreased and is getting close to the concentration in the sea, thus reducing the contribution of diffusion noise. Indeed the drift noise level of the BAB electrode in Fig. 4 is decreasing sharply for shorter time scales, and tends to be better than the CLF electrode for periods of a few hours (Clerc et al., 1997). For long time periods, however, the drift noise level of the BAB electrode is high because this electrode is partly desaturated, indicating that diffusion noise contributes only for small time periods, and electrochemical degradation contributes at long periods.

The AgCl TOK electrode appear from the present experiment as a superior design for measurements in sea water. However, in real measurement conditions, the sea water is not a stable medium as the water vessel used in our experiment, and the two electrodes of one dipole do not sit at the same precise point. The question then arises of the sensitivity of the electrode to temperature variations or changes in water salinity. A change of salinity of 1% would give in principle a change in potential of about 0.25 mV (Junge, 1990) but the sensitivity of the TOK electrodes to salinity changes might be reduced by the low porosity of the ceramic casing. The CLF-Na electrode which shows larger drifts than the TOK electrodes in Fig. 4 should be in contrast virtually insensitive to changes in salinity. For a precise SP monitoring experiment in sea water, it may be of interest to complement an array of Ag/AgCl electrodes by some CLF-Na dipoles.

3.2 Analysis of the variations observed with electric dipoles in the soil

Garchy is located on the edge of the Parisian sedimentary basin. The experiment was set-up in a field which is part of a large open space without trees. The woods start 50 m south of the southern hole line. This field was not used for agricultural purpose for more than 20 years, and was only mown once a year. The grass of the field was cut again just before the experiment but weeds and brambles grew wildly during the spring and early summer.

Callovo-oxfordian Jurassic calcareous layers are found a few meters below the surface. The amount of rocks and clay however varies from point to point, as was revealed by the digging of the holes. The heterogeneous nature of the electrode field was confirmed by a shallow resistivity map (Fig. 5(a)), which identified a conductive zone on the western side of the field. No SP anomaly however has been observed in the field. The SP potentials remain within the measurement error (a few mV) with respect to a central point, and this was checked several times over the one-year data acquisition period.

This electrical structure of the subsurface has an important consequence on the overall scale of the induced MT electric field. In Fig. 5(b), the intensity of the observed MT signal on each dipole is shown relative to a reference dipole located in the center (CLF-Na dipole, hole 23). The MT signal intensity on the various dipoles can change by about 20% from one side to the other side of the field, an illustration of the static shift effect (Jones, 1988).

For the problem of long time stability of the electrodes studied in the present paper, the external MT variations have a small impact, but they are subtracted from the observed signals for completeness. A MT transfer function is therefore calculated using a robust remote reference algorithm (Chave and Thomson, 1989), the remote reference site being taken in Chambon-la-Forêt, one hundred twenty kilometers north-west of Garchy. A theoretical induced signal is then calculated using the obtained transfer function and the observed magnetic signal. This theoretical signal was then subtracted from all dipoles.

An alternative way to eliminate the external MT variation is to subtract from the studied dipole the signals from one reference dipole, taking into account the scaling introduced by static shift and measured in Fig. 5(b). This alternative method is more powerful to eliminate MT variations at all frequencies, and easy to implement, and it has also been used in the present study.
Some transient signals were also observed on all dipoles. These signals, probably associated with activity of large farms in the neighbourhood of Garchy, were rather infrequent and were not corrected for.

3.3 General observations for dipoles in the soil

Some electrode designs exhibit instabilities. These instabilities are transient signals that are observed on one dipole only, and hence are signals produced in one of the electrodes of the dipole, or in its immediate neighbourhood. Examples of such instabilities are shown in Fig. 6. For a given dipole, the amplitude of the instabilities, their time scales and signs can vary with time. In a few cases, instabilities were related to the activity of field mouses at night and burrows. The cause
Fig. 6. Examples of electrode instabilities. The quantity shown is the difference between the tested dipole and the reference dipole of channel 7 (CLF-Na, hole 23) scaled according to Fig. 5.
of most electrode instabilities however is not clear and there is no obvious triggering process like rainfall. These instabilities tend to be observed frequently (once a day or so) for electrodes where corrosion has been seen after undigging and the electrode was dismantled (IST) or electrodes with absorbed electrolyte in plaster during dry soil conditions (PHO or BLC electrodes). An explanation for the instabilities could be a chemical evolution of the contact surface between the metal rod and the surrounding electrolyte support.

Some clear differences appear between dipoles at long periods. Some dipoles exhibit drifts of the order of several mV over one day, of more than 10 mV over one year, or have large diurnal effects.

In particular, designs with Cu/CuSO₄ and liquid electrolyte (POT, KOL) or the liquid electrolyte Pb/PbCl₂ EDI dipole are unstable. This can be due to corrosion at the level of the liquid-air interface near the central metal rod. Actually, a design with a coated central Copper rod shows significant improvements (Nascimento in Clerc et al., 1997). Also, the tightness of the liquid electrolyte vessel can affect the stability and should be checked carefully. Intermittent electrical noise can be related to liquid leakage as well.

The installation with a bucket was systematically compared with an installation without bucket for MOS electrodes (Fig. 2, lines 15 and 16) and PHO electrodes (lines 1 and 39). The installation with a bucket was unambiguously better, confirming previous studies (Bogorodsky and Bogorodsky, 1996). The potentials of MOS and PHO electrodes installed without bucket had changed over one year by more than 20 mV from a fixed reference, and more than 10 mV in a given electrode pair, whereas the potentials of electrodes installed in a bucket had stayed at their original values within less than 3 mV. In fact, MOS electrodes desaturate within 3 months if installed without a bucket, and in even less time in soaked soil conditions.

Daily averages for the few reasonably stable dipoles are shown in Fig. 7 for the whole data acquisition year. No clear common SP variations appear. The observed variations must then largely reflect the evolution of the electrodes, or heterogeneous SP effects of near surface origin.

Also shown are the rainfall, the soil moisture and the soil temperature at a depth of 52 cm. One can see from the soil moisture data (recorded at a depth of 50 cm) that the rain and the thunderstorms during the summer did not increase the soil moisture while the soil moisture dropped to saturation after day 280. One can then conclude that a summer with dry soil was followed by a wet autumn and winter during which the soil was soaked with water. The succession of these two extreme conditions (quite unusual otherwise in Garchy) has been very useful for the experiment, as the behaviour of the electrodes are very different in dry and soaked soil conditions.

During the dry soil season, cracking of the soil introduced contact problems for electrodes installed without salted mud. In particular, STR electrodes showed some instabilities. In general, electrodes with liquid electrolyte had to be refilled often, and the slight percolation of the fluid outside the electrode was not sufficient to keep the soil humidity high at the contact point. Delays in refilling the LEI electrodes degraded the performances of these otherwise stable probes, and introduced extra restabilisation times to reach a new equilibrium. For some extreme cases, the electrodes were damaged by the dry soil conditions, they had to be changed, or reinstalled after treatment in the laboratory.

The typical linear drifts are shown as a function of time scale in Fig. 8, separately for the dry soil season and the soaked soil season, using the same representation as in Fig. 4. One has to keep in mind however that the drifts observed in the soil are in general time dependent, and are more complicated to quantify than in the salted water vessel. Figure 4 therefore gives only an indication of the performances of the electrodes, and a way to compare the various dipoles between each other.

The potentials in Figs. 7 and 8 have not been corrected for temperature effects. Potential variations for some dipoles seem to be correlated with the temperature at times, especially during the dry soil season. This is particularly true for the CAM dipoles for example. However, it is
Fig. 7. Daily averages of some of the more stable dipoles in the soil during the Garchy electrode experiment. The signals have been corrected for the small MT contribution. The origin of days is January 1, 1995. Note that the CAM dipole v27 is actually in the perpendicular direction (see Fig. 2).
unlikely that the observed variations are due to temperature only. Temperature variations in the soil at periods larger than one week are not attenuated much at the installation depth of the electrodes. These temperature variations can have an effect on the measured potential differences through the temperature coefficients of the electrodes, if the temperature coefficients of the two electrodes of the dipole are not identical or if the installation depth or the thermal diffusivity of the soil are different at both ends. A correction can in principle be undertaken if the temperature coefficient of the electrode is stable with time, and if the temperature at the electrode is known. However, the temperature coefficients of the electrodes tend to be unstable (Clerc et al., 1997). In addition, dipoles with electrodes having similar temperature coefficients did not show the same variations in the potential differences. Pending a better understanding, and in order to avoid mixing temperature effects with other effects affecting the neighbourhood of the electrode and
indirectly related to temperature (like for example root activity near a KCl rich contact point), it was decided not to include any systematic temperature correction at this stage of the analysis.

3.4 The effect of rain and percolating water

One clear phenomenon explaining the features of the potential variations in Figs. 7 and 8 is rainfall. These variations can be understood by looking at the TOK dipole and the CLF-Na dipoles.

As explained before, the TOK electrode is designed for sea measurement and has such a porosity that the internal ion content and concentration is determined by the outside medium. This electrode was also installed in the soil for comparison, using an installation with salted kaolinite mud (Fig. 1(a)). It is observed that the TOK dipole in the soil is quite stable during the dry season, but is dramatically affected by rain, meaning that the surrounding mud has evolved after rainfall.

The CLF-Na dipoles v7 and v8, as well as the difference v7-v8 are shown in Fig. 9. These two dipoles connect electrodes installed in the same hole, in salted kaolinite mud. The difference v7-v8 is smaller than 0.1 mV during the dry season but changes up to 5 mV after a succession of rainfall.

More precisely, the initial difference after installation in the field was -0.7 mV, whereas the potential difference due to the electrodes only was 0.01 mV. At the end of the experiment, the difference had increased to 4.2 mV. This increase was not due to an evolution of the electrode, as the potential due to the electrodes after recovery was measured to be -0.1 mV only. The increase in the difference was therefore due to a real local change in SP of the order of 5 mV. The time structure of this change is given by the v7-v8 curve in Fig. 9. It has a rise time of about 0.2 mV/day and induces an irreversible shift of potential of a few mV.

The variations of the TOK and CLF-Na dipoles after rain point to an evolution of the contact mud after rainfall. The timing demonstrates that the percolation of water in the soil leached a significant quantity of the salt from the contact mud in about two weeks. As the salt was removed, the potential sampled by the electrode through the volume average of the conductive salted zone was changing accordingly. The natural soil has indeed an heterogeneous electrical structure, and SP varies on a few cm distance by a few mV (Ernstson and Scherer, 1986; Clerc et al., 1997).

This mechanism of salt leaching can be confirmed by measuring the resistivity of the contact clay. The resistivity of the contact mud was measured at the end of the experiment to be 4.2 Ωm in hole 23N and 7.1 Ωm in hole 23S (see Fig. 2), whereas the resistivity of the fresh mud is 0.16 Ωm. The Garchy local clay (not including limestone rocks) has a typical resistivity of 5 Ωm.

On the other hand, electrodes installed without salted kaolinite mud (CAM, LEI, STR) were not affected by rainfall.

In addition to this effect due to the drainage and dissolution of salt around the contact point, which has characteristic times of several days or weeks and is related to the installation method, some potential variations are observed immediately after rainfall (Fig. 10). These potential variations appear on all dipoles simultaneously and the size of the variation varies smoothly from point to point in the field in a characteristic and systematic fashion. The rise time is of the order of 1 mV/hour and recovery occurs after 15 to 30 hours. The size of the effect seems to be related to the shallow soil structure as shown in Fig. 5. These potential variations are likely to be electrical signals induced by water percolation (electrokinetic effect). These signals deserve more work, as they could be used for example to monitor the penetration of water in a soil (Clerc et al., 1997).

3.5 Observations of daily variations

Heterogeneous daily variations were also observed, as shown in Fig. 11. These variations, larger than the MT signals, appear during the dry season and were present during most of July 95. These variations could be due to several effects, including temperature effects in the case of
Fig. 9. Daily averages of CLF-Na dipoles during the Garchy electrode experiment. Dipoles v7 and v8 are parallel and in the same holes at both ends. An installation with a salted kaolinite mud was used. The signals have been corrected for the small MT contribution.

some dipoles, but the bulk of the effect in Fig. 11 appears on all dipoles. This effect can not be explained by temperature sensitivities of the amplifiers and filters as they were measured to be negligible. It could be related to a botanical phenomenon indirectly related to temperature, such as evapotranspiration. Indeed some fresh roots were observed near electrode contacts during undigging. The main characteristics of this type of diurnal variations is that dipoles installed in the same way shifted by 2 m have quite different variations, illustrating the local nature of electrical signals, as measured in other cases (Morat and Le Mouël, 1992). These diurnal variations need to be minimized when measuring long period MT signals, in particular in the context of upper mantle conductivity studies.
Fig. 10. Example of quasi-reversible potential variations induced by rainfall. The scale is in mV. Note the different scales of individual tracks. The signals have been corrected for the small MT contribution.
Fig. 11. Example of daily potential variations observed during the summer. The scale is in mV. Note the different scales of individual tracks. The signals have been corrected for the small MT contribution, and hourly averages are plotted.
4. Conclusions

Some first conclusions can be drawn from the one-year Garchy electrode campaign.

In addition to MT signals and few industrial transients, potential variations of electrode sensor origin are observed on the electric dipoles. Some variations and instabilities are related to the electrodes themselves and some to the installation method.

From the electrode and installation effects observed during the experiment, some recommendations for long period electrical measurements can be proposed. A few reliable electrode designs are indeed available. Designs of similar performances include the MOS and the CLF Pb/PbCl₂ electrodes, and the LEI and TOK Ag/AgCl electrodes, the TOK electrode being outstanding in the case of measurements in the sea. Cu/CuSO₄ electrodes are not competitive, with the remarkable exception of one design with kaolinite absorber (STR, Meunier, 1996). No conclusion on the Cd/CdCl₂ couple can be drawn from one design only.

It appears that the metal/metal-ion is not the only determining factor in the overall performance of the electrode. The performances of the electrodes are also defined by the precise practical implementation of the concepts and the details of the design. Liquid electrolyte designs seem to produce good Ag/AgCl electrodes (LEI, CAM), whereas the best combination for Pb/PbCl₂ electrodes seem to be the CLF electrode with kaolinite absorber. It is recommended that future work concentrates on these superior designs and that other designs are not used for precise MT or SP monitoring experiments.

Once a satisfactory electrode is in hand, the actual performances in the field depends also on the installation method in a crucial way. In dry soil or in deserts, it appears necessary to install the electrode in a salted kaolinite mud or in bentonite. In contrast, in soaked soil with water circulation, a mud with NaCl should not be used. For intermediate conditions, installation in a bucket offers a good compromise for a robust electrical contact. Electrodes for long term monitoring should be buried more than one meter deep.

In addition, because of local SP effects near the electrical potential measurement point, SP monitoring experiments should be designed with enough redundancy and cross-checks, in particular when transient effects are of critical importance, for example earthquake precursory effects. If possible, various installation methods, and electrodes of both types Ag/AgCl and Pb/PbCl₂ should be used.

The Garchy experiment also demonstrates that local soil heterogeneities tend to produce additional SP variations, such as potentials after rainfall or anomalous daily variations. It may be of interest to study these phenomena in more detail, as they might reflect important parameters of the soil or its biological activity.

For a precise SP monitoring experiment, because of these additional heterogeneous SP effects, it would probably be useful to map the shallow resistivity of the measurement points and install electrodes in the most uniform areas. It would also be of importance to establish the local drainage property of the soil in order to select the proper installation method. It could also be interesting to monitor the resistivity of the soil near the installation point at the same time as the SP.

A more detailed discussion of the various recommendations proposed for each application will be presented in the technical report (Clerc et al., 1997).

The conclusions of this study could be refined in future works. It would also be important to test the conclusions of this study in various geophysical and geographical environments over longer periods of time.

The authors acknowledge the support and dedication of the members of the Centre de Recherches Géophysiques of Garchy, and in particular of Pierre Marquis. The experiment could take place thanks to funds received from Institut des Sciences de l'Univers, CNRS, Institut de Physique du Globe, Paris,
Laboratoire de Géophysique, Bruyères-le-Chatel, the National Environment Research Council (U.K.), Thomson-Sintra, Compagnie Générale de Géophysique and Schlumberger Research (France). Pr Steinberg from Université d'Orsay is thanked for his kind analysis of the clays used for the installation of electrodes in the field.

REFERENCES

Bogorodsky, V. M. and M. M. Bogorodsky, Methods and technical means for measuring quasi-constant natural electric fields, in Proceedings of the Workshop "Electrodes", Garchy, April 24–29, 1995, edited by G. Clerc, F. Perrier, G. Petiau, and M. Menvielle, 1996.

Chave, A. D. and D. J. Thomson, Some comments on magnetotelluric response function estimation, Geophys. Res. Let., 94, 14215–14225, 1989.

Choquier, A., Electrodes Impolarisables Pb-PbCl₂, Rapport CNRS-CRG Garchy, 1996.

Clerc, G., The low-drift and low-noise amplifier used for the campaign of intercomparison between electrodes (Garchy, 1995–1996), in Proceedings of the Workshop "Electrodes", Garchy, April 24–29, 1995, edited by G. Clerc, F. Perrier, G. Petiau, and M. Menvielle, 1996.

Clerc, G. et al., The Garchy Electrode Experiment: Technical Report, in preparation, 1997.

Erkul, E. and A. Müller, Experiences with different electrodes in continuous magnetotelluric measurements at the north anatolian fault zone, in Proceedings of the Workshop "Electrodes", Garchy, April 24–29, 1995, edited by G. Clerc, F. Perrier, G. Petiau, and M. Menvielle, 1996.

Ernstson, K. and H. U. Scherer, Self-potential variations with time and their relation to hydrogeologic and meteorological parameters, Geophysics, 51, 1967–1977, 1986.

Filloux, J. H., Instrumentation and experimental methods for oceanic studies, in Geomagnetism, vol. 1, ch. 3, pp. 143–248, London Academic Press, 1987.

Fujinawa, Y., T. Kumagai, and K. Takahashi, A study of anomalous underground electric field variations associated with a volcanic eruption, Geophys. Res. Let., 19, 9–12, 1992.

Hamano, Y., T. Yukutake, and J. Segawa, Development of new silver-silver chloride electrodes for ocean bottom electrometers, in Proceedings of Conductivity Anomaly Symposium, Japan, 251–258, 1984 (in Japanese).

Harned, H. S. and B. B. Owen, The Physical Chemistry of Electrolytic Solutions, Reinhold, New-York, 1958.

Hashimoto, T. and Y. Tanaka, A large self-potential anomaly on Unzen volcano, Shimabara Peninsula, Kyushu island, Japan, Geophys. Res. Let., 22, 191–194, 1995.

Henderson, P., Z. Phys. Chem., 39, 161, 1907.

Henderson, P., Z. Phys. Chem., 63, 325, 1908.

Jones, A. G., Static shift of magnetotelluric data and its removal in a sedimentary basin environment, Geophysics, 53, 967–978, 1988.

Junge, A., A new telluric KCl probe using Filloux's AgAgCl electrode, Pageoph, 134, 589–598, 1990.

Larsen, J. C., Transport and heat flux of the Florida Current at 27°N derived from cross-stream voltages and profiling data: theory and observations, Phil. Trans. R. Soc. Lond., 338, 169–236, 1992.

Mennier, J. M., Diurnal earthcurrents with short lines and unpolarized copper-copper sulfate-kaolinite electrodes, in Proceedings of the Workshop "Electrodes", Garchy, April 24–29, 1995, edited by G. Clerc, F. Perrier, G. Petiau, and M. Menvielle, 1996.

Morat, P. and J. L. Le Mouël, Signaux électriques engendrés par des variations de contrainte dans des roches poreuses non saturées, C. R. Acad. Sci. Paris, 315, 955–962, 1992.

Park, S. K., M. J. S. Johnston, T. R. Madden, and H. F. Morrison, Electromagnetic precursors to earthquakes in the ULF band: A review of observations and mechanisms, Rev. Geophys., 31, 117–132, 1993.

Petiau, G., Pb/PbCl₂ electrodes: second generation, in Proceedings of the Workshop "Electrodes", Garchy, April 24–29, 1995, edited by G. Clerc, F. Perrier, G. Petiau, and M. Menvielle, 1996.

Petiau, G. and A. Dupis, Noise, temperature coefficient, and long time stability of electrodes for telluric observations, Geophys. Prospect., 28, 702–804, 1980.

Ruzié, G., Comparison between different electrodes for long term measurements, in Proceedings of the Workshop "Electrodes", Garchy, April 24–29, 1995, edited by G. Clerc, F. Perrier, G. Petiau, and M. Menvielle, 1996.

Zlotnicki, J., S. Michel, and C. Ammen, Anomalies de Polarisation Spontanée et Systèmes Convectifs sur le Volcan du Piton de la Fournaise (Ile de la Réunion, France), C. R. Acad. Sci. Paris, 318, 1325–1331, 1994.